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UNITED STATES DISTRICT COURT

DISTRICT OF RHODE ISLAND

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EMHART INDUSTRIES, INC.,	)	
	)	
Plaintiff,	)	
	)	
vs.	)	Civil Action No. 02-053 S
	)	
HOME INSURANCE COMPANY, INSURANCE COMPANY OF NORTH AMERICA, LIBERTY MUTUAL INSURANCE COMPANY, NORTH RIVER INSURANCE COMPANY, ONEBEACON AMERICA INSURANCE COMPANY, and UNITED STATES FIRE INSURANCE COMPANY,	)	
	)	
Defendants.	)	

DEPOSITION OF THOMAS F. CLEARY

Monday, February 10, 2003

Mendocino, California

Reported by:
LUEL J. SIMSON, CSR No. 4720

SIMSON REPORTING
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Windsor, California 95492
(707) 838-6724

BE IT REMEMBERED THAT, pursuant to Notice, on Monday, February 10, 2003, commencing at the hour of 9:03 a.m., thereof, at the Mendocino Hotel, 45080 Main Street, Mendocino, California, before me, LUEL J. SIMSON, CSR No. 4720, State of California, personally appeared:

THOMAS F. CLEARY,

called as a witness by the Plaintiff; who, having been duly sworn by me, was thereupon examined and testified as is hereinafter set forth:

---oOo---

A P P E A R A N C E S

For the Plaintiff:

Law Offices of WILLCOX, PIROZZOLO & McCARTHY
50 Federal Street
Boston, Massachusetts 02110

By: RICHARD L. BINDER, Esq.

For the Defendant, LIBERTY MUTUAL INSURANCE COMPANY:

Law Offices of HOLLAND & KNIGHT
50 California Street, Suite 2800
San Francisco, California 94111

By: H. LARRY ELAM, III, Esq.

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A P P E A R A N C E S--(Cont'd.)

For the Defendant, NORTH RIVER INSURANCE COMPANY:

Law Offices of LUCE, FORWARD, HAMILTON & SCRIPPS
600 West Broadway, Suite 2600
San Diego, California 92101

By: ANDREW R. McCLOSKEY, Esq.

For the Defendant, ONEBEACON AMERICA INSURANCE COMPANY:

Law Offices of HERMES, NETBURN, O'CONNOR & SPEARING
111 Devonshire Street
Boston, Massachusetts 02109

By: KEVIN J. O'CONNOR, Esq.
(Via Telephone)

For the Witness:

JOHN C. PORTER, Esq.
45351 South Caspar Drive
Mendocino, California 95460

Also Present:

Law Offices of SWIDLER, BERLIN, SHEREFF & FRIEDMAN
3000 K Street, N.W.
Suite 300
Washington, D.C. 20007

By: LAURA A. FORD, Esq.

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THOMAS F. CLEARY,

having been first duly sworn, was

examined and testified as follows:

EXAMINATION

BY MR. BINDER:

Q. Okay, Mr. Cleary, could you please state your name and address.

A. My name is Thomas F. Cleary. I live at 45451 South Caspar Drive; Mendocino, California, 95460.

Q. And you are here pursuant to a Deposition Subpoena?

A. Yes.

Q. Could you briefly describe, if you would, your educational background.

A. I'm a graduate of the Chemistry School of Rutgers University. I was employed at companies such as Merck & Company --

MR. O'CONNOR: If Mr. Cleary is talking, I can hear nothing.

THE WITNESS: Boy, that's a surprise.

MR. BINDER: Let's go off the record.

(Off the record; record read.)

THE WITNESS: Merck & Company, E.R. Squibb, Bayer. Then I got out of strictly commercial or rather

technical work and into work that was partly technical and partly commercial in the interest of making a better living.

And I was in that kind of activity for about 20 years. I called on virtually every pharmaceutical company with a recognizable name during that period. I developed processes for and arranged the manufacturing facilities for a number of them.

I then left that employer, left New York, started a consulting firm of my own, continued to do this kind of work for people abroad. I worked in France, Italy, Turkey, Israel, Mexico. I still am connected with a Mexican firm as a general consultant and do process development work for them.

My main technical ability is the development of chemical processes, of which I have developed many dozens, some of which have resulted in profitable commercial production. I'm still interested in this field, still in contact with my Mexican attachments. And what else can I tell you?

MR. BINDER: Q. Okay. Let me go back over a couple of these things and maybe you can fill in a little more detail where it comes up.

A. Sure.

Q. When did you graduate from Rutgers?

A. In 1938.

Q. And what degree did you obtain?

A. I beg your pardon?

Q. What degree did you obtain?

A. I have a B.S. in chemistry.

Q. And you mentioned that you did mostly technical work for Merck and Squibb and Bayer. Could you explain briefly what some of that technical work entailed.

A. Yes. At Squibb, in particular, I developed processes for making sulfa drugs, for isolating the active substance of curare, for purifying penicillin. That's about the headlines of the work.

Q. Have you taken any -- did you take any postgraduate education?

A. No.

Q. Are you an organic chemist?

A. Yes.

Q. And just for the record, what is an organic chemist?

A. Well, an organic chemist is one whose work is preoccupied with, I would have to say, carbon-based molecules.

Q. Okay. And your period when you were doing mostly technical work for Merck, Squibb and Bayer, would that have been for approximately 20 years after you graduated

from Rutgers?

A. More like about 14 years, I would say.

Q. Take us to about 1952?

A. About that, yes.

Q. And then when you began your work that was partly technical and partly commercial, did you work for a particular company?

A. I worked mainly for a company called now Centerchem.

Q. Could you briefly describe what the business of Centerchem was during that period.

A. Yes. Centerchem was principally a U.S. representative, a sales representative, for a very large number of mainly European manufacturers of pharmaceutical ingredients. They were located in almost every country in Europe, also in Indonesia. And from time to time, I visited every one of them, except the one in Indonesia. And, on occasion, I took some of their representatives around the United States to visit some of their customers. And that included contacts with virtually every pharmaceutical company of note at that time.

Q. For approximately how long were you working at Centerchem?

A. Twenty years.

Q. So that would take us from about 1952 to 1972?

A. No. That would take us from 1960 to 1978, about.

Q. Okay. And can you fill us in a little bit about what you were doing, what your employment was, between 1952 and 1960?

A. Let me see. I worked for Merck for four years and for Squibb for four years. The Bayer association was somewhat distant. It resulted from a visit to Germany that I made in around 1949.

And the result of that visit was that an American group of interested people who had somehow sought me out as their technical person and representative, was the establishment of a Bayer-designed plant in the United States, which I was responsible for setting up and getting in motion. And then for a while, I was the director of research for this company, which I happened to name, as a matter of fact. It was called Chemagro Corporation.

And I did many things for them. I visited practically every agricultural chemical school in the country promoting Chemagro's products. There came a time when we were short of cash and, in an effort to adjust my income upward from where -- to where it had been, I did a great many odd jobs in the chemistry business.

I was pretty well known and my -- I had a good reputation for developing chemical processes, and I had no problem whatsoever finding additional work here and there

to fill in my main duties for Chemagro Corporation, for which I remained a board -- on the board of directors. And finally resigned totally in order to go to work for Centerchem full time.

MR. ELAM: I'd just like to raise an objection. The response was nonresponsive to the question, and I'd like to move to strike. Just for the record.

THE WITNESS: What is the objection?

MR. ELAM: Mr. Cleary, it's just for the record down the line, should any party want to use this deposition transcript at trial in Rhode Island. So it has nothing to do with your testimony. It's just for the record.

THE WITNESS: I still don't understand your point.

MR. BINDER: I think what he was trying to say, Mr. Cleary -- and correct me if I'm wrong, Mr. Elam -- is that you provided somewhat more information than what I had asked for, and he wanted you to -- he's objecting on the grounds that you didn't sort of confine your response to what I had asked.

Is that a fair statement, Mr. Elam?

MR. ELAM: That's a fair statement. Only to the extent that it's just for -- it's a legal issue. It's not for the content of what you provided. It's just a legal

issue.

THE WITNESS: Well, you can strike out any part of it that you want to.

MR. ELAM: Right.

MR. BINDER: And, ultimately, at trial if this is raised again, the judge will decide what part to be -- if any, to be stricken.

THE WITNESS: That's all right with me. Mold it any way you want to. I'm telling you -- I'm overtelling you what's going on, what had gone on.

MR. BINDER: Okay.

Q. Now, during the -- when you went to Centerchem in 1960, what was your initial position at Centerchem?

A. I don't think it had a title. The fact is I was the only technical person there, and I brought a special skill to the organization, which was that I knew a lot more of the chemistry of the products we were selling.

I was also in a position to continue a kind of work which added substantially to the company's revenue. That is to say, that I was very well known throughout the chemical -- throughout the pharmaceutical industry. I could go into them and discover what new products they had planned. I could have recourse to chemical laboratories of friends of mine who frequently let me use them for whatever purpose I needed.

I could develop chemical processes, I could go back to the pharmaceutical companies for -- with whom I was acquainted, tell them that I was -- if they needed production in this particular item, that I was prepared to help in supplying such an item. And this happened many times.

Q. Okay. From your beginning as the chief technical person, did you also obtain other positions at Centerchem?

A. Yes. I was CEO of the company when I left.

Q. Okay. So that would have been in 197- --

A. '78.

Q. Okay. And for how long were you CEO of the company?

A. About two years.

Q. About 1976 to 1978?

A. Something like that.

Q. And did your duties at Centerchem include calling on small chemical companies?

A. Oh, yes; I still did the same kind of work.

Q. And did that include working out brokerage arrangements where you arranged for a small chemical company to make a product to meet the needs of another company?

A. Yes.

Q. In the course of that employment, did you have

occasion to come into contact with a company called Metro-Atlantic, Inc.?

A. Yes, I did. And the story of that is very simple. As a matter of fact, it happened as far back as 1960 when I was first employed there.

The company had been selling a chemical which is used in the textile business as what is known as an antibleeding agent, which means that when a fabric is dyed, the application of the substance beforehand prevents the dye from running over into the intended -- beyond the intended pattern.

This chemical was made in New Jersey, in Sayreville, New Jersey, by a small company who went out of business, and it was then my obligation, more or less, to find another source for it. Because we had been selling it for them, particularly to a firm who are still in that general business of dye stuff and dye stuff related chemicals, a company called Crompton and Knowles, which was located in Paterson, New Jersey. And we were a reseller of this substance, which is called meta-nitrobenzene sulfonate -- sodium sulfonate.

So I had to look for another source to keep our customer attached to us, and that is how I came to look up Metro-Atlantic and become acquainted with Joseph Buonanno. He was quite happy to supply our resale requirements of

this chemical, so the business continued.

Q. Okay.

A. And as the business continued, I became more and more acquainted and friendly with Joseph Buonanno, which led to our discussion of his being able to do some of this custom manufacturing in which I was already heavily involved.

Q. Okay. Could I just ask you a couple more detailed questions about this?

A. Sure.

Q. Would I be correct in understanding that you -- you originally contacted Metro-Atlantic to determine if they could manufacture this antibleeding agent for --

A. They were already manufacturing it. They were already manufacturing it.

Q. And they became another source of supply --

A. That's right.

Q. -- for your customer?

A. They were glad to have another customer which at that time was unknown to them. In other words, they were not selling it directly to this customer, this customer was not known to them. They were glad to have us as an intermediary to this customer, which was Crompton and Knowles.

Q. And as a broker in that arrangement, your company

received some type of a commission?

A. Yes, right.

Q. I guess I forgot to ask this earlier, but are you a named inventor on any United States patents?

A. Oh, many, yes.

Q. And in the '50s and '60s, were you familiar with anti -- products known as antigermicidal soaps?

A. Oh, yes, yeah.

Q. Could you explain your familiarity with those products.

A. The fact is that I used them. One was Dial soap, which was the largest -- well, there were two principal users of such materials. One was Dial, which is still using one which is not hexachlorophene. The other was pHisoHex, which was manufactured by Winthrop Sterling [sic]. Between those two companies, they probably consumed over 90 percent of all of the hexachlorophene that was manufactured.

Q. I'm sorry; did both Dial and pHisoHex use hexachlorophene?

A. Yes. Dial contained 2 percent of it on a weight basis; and I don't know how much was contained in pHisoHex, but it was at least 2 percent.

Q. Okay. And who was the manufacturer of Dial at that period?

A. The same as is organized now. Dial Corporation of Phoenix, Arizona.

Q. And in your knowledge of germicidal soaps, did you become aware of the properties that were desirable in germicidal soaps?

A. I certainly did. As a matter of fact, one of the subjobs that I had was a competitor of Givaudan in many areas and wanted very eagerly to develop a competitive compound, and I did a great deal of work in that area. None of which was particularly successful.

Q. When you say "Givaudan," was Givaudan the manufacturer of the --

A. Givaudan was the inventor --

Q. Of hexachlorophene?

A. -- in the early 1940s of hexachlorophene. And subsequently, up through the years 1957 -- you see, there are several kinds of patents. One of them, primarily, is a composition of matter patent, which applies to the structure of the chemical itself.

Secondly, there is a patent which is a use patent, which, in this case, would apply to the reduction of or removal of bacteria from the skin. And there are formulation patents. There are process patents.

A process patent is different from a composition of matter patent because, while the composition of matter

patent describes the molecular construction of a given substance, it doesn't necessarily describe any method of making it. A process patent describes the method of making it, and there can be many of them as applied to a single composition patent. And Givaudan continued to issue process patents on hexachlorophene up to at least 1957.

Q. And, Mr. Cleary, were you the inventor of a patent in 1957 called -- one of the inventors of a patent in 1957 called, "Germicidal Soaps Composition"?

A. I was only a single inventor on any patent that had to do with my name.

Oh, this is something else. This is one of my odd jobs. I'd almost forgotten this one. This is the only patent in which my name appears with other names, and that was kind of a courtesy because this was the company that I worked with half time to augment my income. I knew them for several years. Actually, it was Wenneis and the other guy, Chodroff, who invented this compound, and they threw me into here as kind of a courtesy because I had done a lot of work on the field that didn't amount to anything.

MR. BINDER: Okay. Let the record reflect that I'll ask the reporter to mark as Exhibit 1 a copy of the United States Letters Patent 2,814,597.

Q. And that's what you were talking about when you answered my last question. Correct, Mr. Cleary?

A. Yes, that's it. Yes.

(Plaintiff's Exhibit No. 1 was marked for identification.)

MR. BINDER: Q. Exhibit 1, is it okay if I refer to this by the last three numbers, as the 597 patent?

A. I don't even recognize the numbers any longer.

Q. Okay. (Provides document to the witness.)

It's a patent entitled, "Germicidal Soaps Composition."

A. Well, this is the same one you showed me.

Q. Yes, right. Okay. Exhibit 1 lists in the first column several desirable qualities of germicidal soaps.

A. Uh-huh.

Q. One of those is that a germicidal soap should be nontoxic. Is that a correct statement?

A. Well, you know, in these days, the properties of materials intended for purposes like this were superficial compared to what they are today. This compound -- I worked part time for this company in order to augment my income. I was still principally employed by Centerchem.

Centerchem had some friends in this company, they set me up with some part-time work which I did on

Saturdays and Sundays and after school and so on. There is only one company that I know of that actually put this compound, sight unseen, into one of their products, which was Avon Laboratories. And all I can say is that, today, this compound would never get anyplace in this field.

Q. In any event, Exhibit 1 is a copy of a patent --

A. Yes.

Q. -- that was issued to you, among others.

A. Yes.

Q. And did you later begin work on developing a patent for a process for manufacturing hexachlorophene?

A. Yes, I did.

Q. And could you describe, generally, how you went about the initial work in developing that patent.

A. Yes. Before I became employed by Centerchem, I was already contemplating the desirability of developing processes for items such as hexachlorophene, which were monopolies covered by patents which were, to my judgment, not extremely good patents. And I started to work on hexachlorophene some years, probably, maybe two or three years, before I joined Centerchem. And it was always my -- the attraction of hexachlorophene was simply that it had been a monopoly for almost 20 years.

Q. A monopoly because Givaudan had a patent?

A. Yes. It was used by hundreds of customers, not

in large quantities. The large quantities being used by Dial and by Sterling Winthrop. But many, many dozens of smaller companies had small products which contained hexachlorophene. It was kind of a signature element of many, many things that were used for skin application, beauty creams, eczema treatments, stuff like that.

So I worked on hexachlorophene -- there are very tricky chemical aspects to the manufacture of hexachlorophene which one can only determine by experimental work of trying to make the substance in the laboratory. And one of them, the primary one, is that in order to get good yields of a good product, you need to start with a raw material -- namely, 2,4,5-trichlorophenol -- which is very high in purity.

Another important aspect of manufacturing it is that the proportions of the reaction -- the reactants that you use in this preparation have to be exact with relationship to one another. If there is too much of one and not enough of another, why the results are not good, the yield is not good, the quality is not good; and, accordingly, the cost is bad and the customer is not interested.

Q. Okay. And I'm going to show you a copy of United States Letters Patent No. 3,456,020, entitled, "Production of 2,2'- methylene bis (3,4,6-trichlorophenol)," which --

A. That's the full chemical name for hexachlorophene.

Q. -- lists you as the inventor. Is this a copy --

A. Hexachlorophene is just a trivial name --

Q. Excuse me a second. I'm going to ask the court reporter to mark this as the next exhibit.

(Plaintiff's Exhibit No. 2 was marked for identification.)

MR. BINDER: Q. Now, Exhibit 2 is a copy of your patent?

A. Yes, indeed.

Q. And is there a common name for the substance described in the patent?

A. Yeah; the common, trivial name is hexachlorophene, yes.

Q. And is Exhibit 2 a copy of the patent that was issued as a result of some of the work that you've just described that you did in hexachlorophene?

A. Yes. Please note that the issue date of these patents is sometimes years and years after the patent was applied for, which, in turn, might be years and years after the actual work was done. So the difference probably in time between the issue date of this patent and the date when the laboratory work was initiated might be as much as 10 years.

Q. Sure. When you -- and this patent, Exhibit 2, is a method of manufacturing hexachlorophene among -- is that correct?

A. Yes.

Q. And the patent involves a two-step method of the production of hexachlorophene; one step involves reacting trichlorophenol and formaldehyde. Is that correct?

A. That's right. That was really the key to the invention.

Q. And the second step in the process is that the -- once that reaction product is created, there is then a condensing process to purify the hexachlorophene. Is that correct?

A. Well, to conclude the reaction. What we discovered -- what I discovered and which nobody at Givaudan, amazingly, never discovered was that it's possible to run this reaction in two discrete steps.

The principal result or the important result of that is that it enables you to adjust the relative amounts of formaldehyde and trichlorophenol that are used in the reaction exactly, which is very important to the yield and the quality of the product. And you do that by performing an initial reaction, which somehow everybody at Givaudan overlooked was taking place, to form an intermediate compound which I was able to isolate.

And at that time, my knowledge of chemistry was so defective, I didn't really know what that compound was. I just knew that it was different and had never been disclosed before anywhere. And this was done by just modifying the addition of some of the reactants and pausing at a certain state and then continuing to conduct the condensation to make the final product.

Q. Am I correct that that new reaction product that you discovered is claimed in Claim 2 of this patent?

A. I don't know just where everything is placed in these patents.

Q. If you'd take a look at Claim 2, is that the claim that talks about --

A. I think so, yes.

Q. Column 4.

A. Here's one in this patent here that says, "...anhydrous hydrogen" -- that's a misprint. That should read -- I don't know why I didn't catch that. That should read, "anhydrous hydrogen chloride." The word "chloride" is left out.

"...and diluted sulfuric acid to form quantitatively and exclusively a compound which has a melting point of 78 degrees centigrade and a chlorine content of 46.5 percent." And so forth and so on.

Now, that is the new compound that I'm speaking

about.

Q. Okay. And you were referring --

A. Although it wasn't given a chemical name because I didn't really know what it was.

Q. And as you were answering that question, you were reading from the patent?

A. Yes.

Q. Now, the -- in addition to a claim on the reaction product, you also had two claims in this patent concerning the method of producing hexachlorophene. Is that correct? Claims 1 and 3, if we look at Columns 3 and 4 on the second page?

A. I don't have the claims here.

Q. The claims are on the second page, Mr. Cleary.

A. I'm sorry; I didn't really know I had two sheets here. Oh, yeah.

Q. Am I correct that Claims 1 and 3 are a method of producing hexachlorophene?

A. Yeah.

Q. Okay. Now, the method of producing hexachlorophene included, among other things, the use of trichlorophenol. Is that correct?

A. Well, that was indispensable. That's the starting material.

Q. That's the starting material for hexachlorophene.

A. That's right.

Q. And when you began the research work that ultimately led to the patent that's Exhibit 2, did you obtain the trichlorophenol from a manufacturer?

A. Well, in those days, believe it or not, there were probably about six places in Manhattan where you could walk in and buy chemicals over the counter without any ID, without any record. One of them was City Chemical Company on 22nd Street, where I could buy trichlorophenol of reasonable purity and work with that.

Many years later, I did extensive work on making trichlorophenol itself, which was intended for other people, including Givaudan. I had a large contract with Givaudan in later years to supply pure trichlorophenol by methods that I subsequently developed which were not patented which were dioxin free.

But unfortunately for me and Givaudan, too, hexachlorophene production, which had resumed after the Vietnam War, was suddenly cut off again by the news of a fatality that had occurred to an infant in France as a result of application of a hexachlorophene-containing salve or something of that nature.

Q. Let's go back to the 1950s and 1960s. Is it correct that in the '50s and '60s, that you -- were you even aware of dioxin in the 1950s and '60s?

A. No.

Q. And you learned of dioxin at some later time, in the '70s or later?

A. Probably -- dioxin was first -- let me give you a little history on making trichlorophenol. Everyone that I know about, which include all of the big name chemical companies, like Monsanto and Dow and Hercules and Diamond Alkali and Thompson Chemical, all made trichlorophenol in the same way.

They put all of the reactants, which were tetrachlorobenzene, sodium hydroxide and methyl alcohol into one container, one vessel, closed it up and then heated it and hoped for the best. And sometimes the best was far from the best because these reactions developed into what are known as runaway reactions, which means that the desired reaction, instead of taking place gradually, took place suddenly with the result that the pressure and temperature inside the vessel increased tremendously. Sometimes to the point where the reaction vessel exploded. This kind of accident occurred with everyone who ever made trichlorophenol on a commercial scale.

Q. Sure. But going back to the 1950s and 1960s, in that time period, you weren't aware of dioxin. Right?

A. No, I was not. Neither was anyone else.

Q. And that awareness developed in the 1970s,

possibly, or even later?

A. I think it developed in the 1970s, because what happened was that Monsanto, in particular, had an accident of the kind I have just been describing, and the result of it was that a number of workers were contacted with or sprayed with or contaminated with the explosive residues from this accident. And one of the physical results of that was that the workers incurred what was described at the time as chloracne, a skin condition obviously resembling acne which was ascribed to the chlorine content of the composition of that particular reactor.

And my understanding is that Monsanto, being more than usually concerned about things of this nature, conducted a long-term study of the health consequences of this accident, including the longevity of the victims, their general state of health, their other health problems. And as I recall, their findings after a significant and consequential period of time was that the long-term health consequences of this accident were not to abbreviate longevity or to cause any chronic problems that showed up many years later.

The dioxin problem probably became exaggerated, if you will, during the Vietnam War when thousands and thousands and thousands of pounds of dioxin were dropped into areas of Vietnam with consequences that are still

being observed there.

Q. When you say "dioxin," do you mean Agent Orange?

A. Well, Agent Orange was a mixture of 2,4,5-trichlorophenoxy acetic acid and 2,4-dichlorophenoxy acetic acid, which were made, respectively, from crude trichlorophenol, such as the material which came out of reactors making this, and dichlorophenol, which was made in a slightly less -- less troublesome way.

But that's what -- Agent Orange was basically 2,4,5-trichlorophenoxy acid made from impure trichlorophenol. All of which, as we now know, contained dioxin.

Q. So it was not until sometime in the '70s or later that it was identified as dioxin?

A. If you will look at a piece of literature which I lent to you -- lent to you or gave to you from the Merck Index, you will find a chronology of toxicological studies that were made on dioxin during the '70s -- mainly from '73 onward -- which describes some of the toxicology of dioxin.

Q. Sure. I appreciate that.

And getting back to your patent, which is Exhibit 2, as I look at the first column, it describes certain advantages of your method of hexachlorophene over the prior -- if we look at Column 1, lines 49 through 69.

Is that correct?

A. Uh-huh.

Q. And was one of the objects of your patent to produce high purity hexachlorophene?

A. Yes, indeed.

Q. And why was that one of the objectives?

A. Well, to appeal to the customer, certainly, for one thing. For another, the specifications outlined at that time in the U.S. Pharmacopeia were quite loose, in our estimation, and they had been formulated mainly by Givaudan, to give themselves a break, I suppose.

But this substance was purchased by people like Sterling Winthrop on the basis of Sterling Winthrop's own specs, which were, at that time, as were most chemical specs, rather meager because of the absence of the kind of sophisticated analytical equipment that's available today. They involved mainly melting point, which is a highly significant property, color, odor, and not much else.

Q. Now, at some point in time, did you work with Metro-Atlantic to develop hexachlorophene made in accordance with your patent that's Exhibit 2?

A. Well, the history of that is that the first, what I call, custom jobs that was done at Metro-Atlantic was done for Eli Lilly & Company in connection with the project called -- or a product called Treflan, which was a

selective pre-emergent weed control substance. More or less the first of its kind that had been developed.

And at that particular time, I had a very close relationship with Eli Lilly. I had access to their technical people, which was unusual at the time, and I recognized that production as a very difficult chemical job and one which, let us say, was not easily developed by the rank and file of other persons, of whom there were many, who were seeking that kind of work. And I developed a key reaction in that process before seriously approaching Lilly with the prospect of doing that work.

Q. Let's put aside Lilly for a moment. And after you worked with Metro-Atlantic on Lilly, did you then work with Metro-Atlantic to develop the kind of hexachlorophene as described in your patent that's Exhibit 2?

A. Yes; I already had that process ready.

Q. And when you worked with Metro-Atlantic on that process, were you acting as a broker to obtain -- with a customer to whom the product could be provided?

A. Yes.

Q. And who was that customer?

A. I had, myself, done a commercial study of that product before discussing it with Metro-Atlantic. I already had some relationships of various kinds with Sterling Winthrop in Rensselaer. I knew their purchasing

agent well. I discussed with him the possible availability of another source of supply, about which he was extremely enthusiastic. He was ready to take every pound we made and to -- sort of to say to Givaudan, "Hey! You're not the boss anymore." I mean, monopolists always make enemies and Givaudan made a few.

Q. So your process would allow Sterling Winthrop to purchase hexachlorophene from Metro-Atlantic rather than Givaudan?

A. Well, along with Givaudan. Metro-Atlantic couldn't supply enough to meet Sterling Winthrop's needs. They were probably the largest user in the country.

Q. When you spoke with the purchasing agent at Sterling Winthrop about the purchase of hexachlorophene from Metro-Atlantic, did you obtain the Sterling Winthrop specification that you mentioned earlier?

A. Oh, yes.

Q. And did you provide that to Metro-Atlantic?

A. Oh, yes.

Q. And at some point, did you have occasion to demonstrate the process that Metro-Atlantic was using for the hexachlorophene to Sterling Winthrop?

A. As a matter of fact, I did. Sterling Winthrop was exceedingly interested in this plant. As a matter of fact, they sent their vice-president of manufacturing down

to examine it. He gave it his blessing.

Q. And when you say --

A. And I went up to Rensselaer and demonstrated the process in their laboratory.

Q. So you demonstrated your process to Sterling Winthrop both at Metro-Atlantic and at Sterling Winthrop's own laboratory --

A. Not at the same time.

Q. I understand, sure.

A. Metro-Atlantic first. And after I got into production, Sterling Winthrop -- Sterling Winthrop expressed an interest in purchasing the process and the plant at one time. That was the occasion in which their vice-president of manufacturing, whose name I don't remember -- he was an advanced middle-aged man at that time -- came down and examined the plant very carefully and gave it his imprimatur.

Q. Okay. That would be the Metro-Atlantic plant?

A. Yes.

Q. And he also saw the Metro-Atlantic process for manufacturing hexachlorophene --

A. Yes. He saw it from me, or his chemist did, in their own laboratory.

Q. So you demonstrated the Metro-Atlantic process to Sterling Winthrop on at least two occasions; once at

Metro-Atlantic and once --

A. No, that's not how it worked. I demonstrated -- before Metro-Atlantic started production, I demonstrated the process at Metro-Atlantic's laboratory, to George Huse, who was their technical director. And subsequently, by some period of time, about which I'm not sure, I traveled to Rensselaer specifically at their request and for the purpose of demonstrating this process to them.

Q. So you first demonstrated the process to George Huse at Metro-Atlantic.

A. That's right.

Q. And then you demonstrated it to Sterling Winthrop in Rensselaer.

A. That's right.

Q. And you demonstrated at Rensselaer the same process that you demonstrated to Mr. Huse.

A. Exactly.

Q. And did Sterling Winthrop, after that process was demonstrated, agree to purchase hexachlorophene from Metro-Atlantic made in accordance with your process?

A. No, I think the timing is not quite that way. They were purchasing commercial quantities of hexachlorophene before those demonstrations took place and before the executive of Sterling Winthrop came down to examine the plant.

Q. So those commercial quantities you mentioned, those would be -- those were quantities that Sterling Winthrop purchased from Metro-Atlantic.

A. Yes.

Q. And then, subsequently, Sterling Winthrop observed the Metro-Atlantic process and continued to purchase.

A. That's right, yes.

Q. Okay. And Sterling Winthrop observed the Metro-Atlantic process both at Metro-Atlantic and at Sterling's own laboratory in Rensselaer.

A. That's right. That's right.

Q. Okay. And you mentioned that the process -- you showed your patented process for hexachlorophene to George Huse of Metro-Atlantic. Is that correct?

A. That's right.

Q. And did you then assist Metro-Atlantic at all in the development and implementation of that process?

A. To a very minor extent. George Huse was an extremely competent chemical engineer. He had been responsible for setting up very sophisticated operations for Metro-Atlantic. He had been there for many years. He was over my shoulder when I was in the lab with him. We discussed the construction and size of the equipment that would be needed for various operations, but the

installation of it and the operation of it was his responsibility.

Q. Sure. In essence, you showed Mr. [illegible] process and then he worked on the commercial equip[illegible] implement that on a commercial basis?

A. That's right.

Q. And when Mr. Huse had succeeded in implementing that process, did you see the location where Metro-Atlantic manufactured the hexachlorophene?

A. Oh, yes.

Q. Did you see that on a number of occasions?

A. Yes.

MR. BINDER: I'm going to ask the reporter to mark, I guess a series of exhibits. And I'm going to ask the reporter to mark as Exhibit 3 a microfilmed copy of an article from the Providence Sunday Journal Business Weekly dated May 30, 1965, which has production numbers 12000 -- SBSF 12110 through SBSF 12116.

I'm going to then ask the reporter to mark as the next exhibit an enlarged copy of that same article that was photographed from the original newspaper.

And I'm going to ask the reporter to then mark as the following exhibit an enlargement of a photograph from an article entitled -- which has above -- below the photograph, "Upper level of new hexachlorophene plant at

Metro-Atlantic, Inc."

And as the next exhibit in this sequence, another photograph.

Why don't we just mark these three and take a break for a second.

(Off the record.)

(Plaintiff's Exhibit Nos. 3-5 were marked for identification.)

MR. BINDER: And then as the last exhibit in the sequence, an enlargement of another photograph from that newspaper article entitled, "Large perforate centrifuge located in new plant provides company a means of crystal recovery."

(Plaintiff's Exhibit No. 6 was marked for identification.)

MR. BINDER: Okay.

Q. I'm going to ask you -- I guess I want to ask you, first of all, to look at Exhibit 5, please.

A. Yes.

Q. Can you identify what is depicted in Exhibit 5?

A. Am I looking at Exhibit 5 here?

Q. Yes, you are.

MR. McCLOSKEY: Excuse me, Counsel. I don't think we got Exhibit 5 down at this end of the table.

THE WITNESS: Well, you could call this an

all-purpose organic synthesis plant. Something that Saddam Hussein could make weapons of mass destruction in.

MR. BINDER: Q. Anyway, putting the levity of a not-so-funny subject to one side, does Exhibit 5 show a chemical plant that you've seen before?

A. Well, I guess so. I've seen lots of chemical plants that look like that.

Q. Okay. And you note that below Exhibit 5, it reads, "Upper level of new hexachlorophene plant at Metro-Atlantic, Inc."?

A. Oh, yeah. Yeah.

Q. And is that a -- does that appear to be an accurate depiction of the chemical plant at Metro-Atlantic, Inc., as you saw it?

A. Well, that's a long time ago but there's no reason why it couldn't be.

Q. Okay. And is it your best recollection that it is an accurate depiction?

MR. PORTER: He said it could be, not that it is.

MR. BINDER: I know. That's why I'm following up a bit to see whether or not it is.

THE WITNESS: It could be. I can't place the function of every piece of equipment in there. But as chemical plants go, that was extremely simple. And, of course, I recognize what a centrifuge is.

MR. BINDER: Q. Centrifuge, you're referring to Exhibit 6.

A. Yes.

Q. Now, going back to Exhibit 5. You see that it depicts a number of. . .

A. Vessels.

Q. A number of vessels.

A. Yeah.

Q. And were vessels of that type used in the manufacture of hexachlorophene at Metro-Atlantic?

A. Well, vessels of that type were used. Vessels of this type generally are all-purpose vessels. There are glass-lined vessels, mainly, and stainless steel vessels which have different purposes and universal purposes. I can tell you pretty much what the hexachlorophene process was that might have fit into these vessels.

Q. Could you do so, please.

A. Well, first of all, the crude trichlorophenol that was shipped from Diamond Alkali in Newark was treated with chemicals, of which I think I supplied you a list in one of those folders, in order to purify it. And it was then extracted into perchloroethylene. And then it was heated to a certain temperature and formaldehyde was added to it and sulfuric acid as a condensing agent was added piecemeal through that.

And upon completion of the reaction -- this is where we had some problems, of which I assisted in solving. Inevitably, almost any chemical reaction will develop some undesirable color. And in order to remove color, you usually do it with special kinds of charcoal which absorb the color and which then has to be filtered out. And at that point, the reaction product, which, in this case, was hexachlorophene, is in solution, hot in the perchloroethylene. And in order for the colorizing agent, the charcoal, to be effective, it's treated hot, while the substance is still in solution.

And then you filter that out by way of a filter press, which is a group of leaves, I guess you could call them, which are covered with a filter medium, which might be some synthetic substance or it might be ordinary cloth or it might be anything capable of retaining the charcoal that you're trying to filter out of there.

But that reaction mixture contained some globules of sulfuric acid, and they would make holes in the filter cloth and the charcoal would come through. Which, of course, was no good. So we would have to put that stuff back where it came from, clean up the filter press, put some new filter cloth in it, and somehow get rid of the acid that was making those little holes.

So I suggested putting a little calcium carbonate

in there before the filtration was done to neutralize the sulfuric acid. And, lo and behold, that worked.

And then that clear solution, which was almost colorless, was put into a crystallizing vessel, which was made, I believe, out of stainless steel, and it was cooled down slowly in order to get the desired size of crystals. And, finally, the product which had crystallized was filtered out in that centrifuge. I think the same one that was used to separate the purified trichlorophenol. After appropriate cleaning up, of course.

And then the hexachlorophene, which still had a little bit of solvent in it after centrifuging, was put in the dryer and the so-called mother liquor, which is the filtrate you get from crystals, was very easy to recover because perchloroethylene and water form what is known as a constant boiling mixture. And all you have to do is heat it up with water. And in constant boiling mixtures, the boiling point of each of the two constituents is lower than that of either of the substances alone. And it's possible to recover the solvent in full by distilling off this constant boiling mixture.

And, of course, some product remained dissolved in it, which is inevitable, which was rather impure, but we had a customer for the impure stuff, too. Which was Kalo Laboratories of Kansas City, who used it as a seed

disinfectant or as a pesticide against organisms that attack seeds.

Q. Okay.

A. So we recovered all of the trichlorophenol and all of the hexachlorophene.

Q. So the mechanism of recovering the crystal that is shown, say, in Exhibit 6, the crystal that was recovered, was that the hexachlorophene that was recovered in the centrifuge?

A. Yes.

Q. Does Exhibit 6 depict the process of using a centrifuge to recover crystal?

MR. PORTER: Six, I think, is this one.

THE WITNESS: Whatever it is, it was recovered in the centrifuge. That's for sure.

MR. BINDER: Q. At Metro-Atlantic, the crystal was recovered in the centrifuge.

A. Yes.

Q. And you mentioned that the pure hexachlorophene was developed by your process at Metro-Atlantic, that was sold to Sterling Winthrop?

A. Virtually all of it, yes.

Q. And it was a less pure by-product that was sold to Kalo?

A. Right. I would call it -- it's known in the

trade as the second crop.

Q. What do you mean by "second crop"?

A. Well, the first crop is the good stuff that you take out first, and the second crop is what's left over in the mother liquor.

Q. Okay. So rather than -- so you found some productive use to be made of the second crop.

A. We did.

Q. And it was important that the hexachlorophene that was sent to Sterling Winthrop be pure and meet the Sterling Winthrop specs?

A. That's right.

Q. And Kalo did not have such a rigorous spec?

A. They had no specs at all. They were glad to get anything that contained hexachlorophene.

Q. Now, at the time that Metro-Atlantic was manufacturing hexachlorophene using your process as described in your patent that's Exhibit 2, did you believe that that was a superior method of manufacturing hexachlorophene to any other known method?

A. Well, I thought it was different. Whether it was superior or not would be the judgment of the customer.

Q. But you viewed your -- the goal of your patent, which was Exhibit 2, was to develop a batter way of making hexachlorophene.

A. It was to develop a different way of making hexachlorophene.

Q. And, hopefully, a better one.

A. It was meeting specs.

Q. Meeting specs of someone like Sterling Winthrop?

A. That's right.

Q. Your patented method that Metro-Atlantic was using was better, at least in the sense that there was a two-stage reaction and you didn't have to worry about the problem of boiling over that you described.

A. It solved the balance of formaldehyde and trichlorophenol, which was vital to the quality of the product.

Q. And if I understand your patent correctly, your patent used one mole of trichlorophenol to one mole of -- excuse me. Let me strike that.

Yes. If I understand your patent correctly, your invention involved the use of one mole of formaldehyde and one mole of trichlorophenol; while the previous method used two moles of trichlorophenol to one mole of formaldehyde?

A. No, that's not quite how it worked.

Q. Okay. Could you correct me, then.

A. It used one mole of paraformaldehyde and one mole of trichlorophenol -- no. To start with, you had all of

the trichlorophenol there, two moles. But the formaldehyde reacted with only one mole under the influence of a minor amount of acid. It was after the major amount of condensing agent, which was sulfuric acid, was added, that the second reaction took place. I'll draw you a picture of it, if you want.

Q. Just so the record is clear, what are you drawing now, Mr. Cleary?

A. I'm drawing a reaction between -- okay. Here's one mole of --

MR. PORTER: What is a mole?

THE WITNESS: A molecular weight.

MR. PORTER: Okay.

THE WITNESS: A molecular weight in terms of grams, pounds, or whatever. There's the second mole of --

MR. BINDER: Q. You've now drawn two moles of what?

A. Two moles of trichlorophenol.

Q. Okay. Could we put underneath each one "TCP."

A. (Witness complies.)

Q. Now, could you continue drawing the reaction.

A. Now, the first mole of formaldehyde -- I'm not sure I ever understood this reaction, but what happened was that. . .

Anyway, it went something like that.

Anyway, the formaldehyde all reacted with one mole of trichlorophenol to give that compound whose physical characteristics are described in that patent.

Q. That patent is Exhibit 2.

A. And it was this compound that reacted with the second mole of trichlorophenol to make hexachlorophene.

Q. Okay. You've shown that on this drawing which I'm going to ask be marked as Exhibit 7.

(Plaintiff's Exhibit No. 7 was marked for identification.)

THE WITNESS: I'm not sure what that was. I think I mentioned it somewhere in the patent.

Oh, this is not it.

MR. BINDER: Q. The patent you're looking for is Exhibit 2.

A. I guess so. Yeah.

Well, I wasn't sure what it was then. I don't know whether I'm sure what it is now. But it might have been a reaction product with sulfuric acid. I can't balance that.

Well, that's as far as I can go with that. I haven't thought about it for a long time.

Q. Sure. Okay.

A. But I isolated that compound.

Q. You isolated the --

A. I isolated the compound and characterized it physically. I never had it analyzed by carbon content -- you know, by something.

Q. Okay. Getting --

A. Chlorine content.

Q. Sure. Now, getting back to the way your process was implemented at Metro-Atlantic, am I correct in understanding that Metro-Atlantic purchased the trichlorophenol that it used?

A. That's right, yes.

Q. And they purchased it from Diamond Alkali?

A. Diamond Alkali. Exclusively.

Q. You mentioned earlier, in response to one of my questions, that you had provided me with a document that provides some information about the bill of materials that was used in hexachlorophene. Is that correct?

A. That's something that -- that's the only thing that I have that George Huse put together. That's his composition. And how I came by it, I don't remember. I don't -- I didn't know that I even had it.

Q. Okay. What you're referring to -- I'm going to ask the reporter to mark as Exhibit 8.

(Plaintiff's Exhibit No. 8 was marked for identification.)

MR. BINDER: Q. Mr. Cleary, is Exhibit 8 the

document you were just referring to?

A. Yes.

Q. And could you identify it for the record, please. Is that a document you received from Mr. Huse?

A. Sometime, I must have.

Q. That's a document you produced today -- you produced in response to the subpoena?

A. That I produced?

Q. That you provided to us as a result of the subpoena that we gave you.

A. As a result of your subpoena, I looked through every folder this high (indicating) that I have which refers to many, many things, and I found this, unexpectedly.

Q. You found Exhibit 8, unexpectedly.

Now, Exhibit 8 --

A. It has a date on it, which is nice.

Q. It has a date of June 8, 1964.

A. Yes.

Q. Are you familiar with the term "ZEP," Z-E-P?

A. Yes.

Q. What is ZEP?

A. That was a nickname that we used for the product.

Q. For hexachlorophene?

A. Yes.

Q. A nickname you and Mr. Huse used?

A. Yes.

Q. Now, Exhibit 8 --

A. He made it up. I don't know how, but he made it up.

Q. Now, Exhibit 8 says --

I'm sorry, Counsel, I only have the one copy received from the witness.

It says, "ZEP Manufacture, Phase No. 1."

A. Uh-huh.

Q. Do you know whether there was -- there were further phases in the manufacturing process than just that phase?

A. That was the phase of purifying the trichlorophenol.

Q. Now, this is the trichlorophenol that was purchased from Diamond Alkali?

A. That's right.

Q. And the title "ZEP," once again, refers to hexachlorophene.

A. That's right.

Q. And do you know whether, before Metro-Atlantic obtained trichlorophenol from Diamond Alkali, it provided, either directly or through you, any specifications for the trichlorophenol?

A. I'm not sure I follow your question.

Q. Okay. Did either Metro-Atlantic itself or you, on behalf of Metro-Atlantic, tell Diamond Alkali, "We want a certain grade of trichlorophenol"?

A. No, no. The grade of trichlorophenol that was purchased and was made by Diamond Alkali presumably was relatively uniform and consisted of nothing but the contents of the reactor after they had performed the reaction. It was full of whatever was made in that reaction.

Q. So that was the generic --

A. The spec, if you call it that, for the purified material, or the goal that we aimed for in purifying that material, was a melting point, which I believe was something like 65 to 66 degrees.

Q. That's the melting point for the TCP?

A. But the way -- that's right. But the way we received it was in solution, with no solids. It was a brownish solution that had a trichlorophenol content probably on the order of 20 to 30 percent. The rest being liquid; mainly alcohol and water.

Q. And this trichlorophenol was intended to be used by Metro-Atlantic to develop as part of -- a step to develop a pure hexachlorophene for --

A. That's right.

Q. -- the customer.

A. Because it was cheap to do it that way, and I knew Diamond Alkali well enough myself to engage in conversations leading to that. There was only one pure trichlorophenol available in the market. It was made by Hooker Chemical Company, who became part of some big oil company.

Hooker had an exclusive arrangement with Givaudan to sell to Givaudan pure, or alleged pure, trichlorophenol.

Q. So Metro-Atlantic was precluded from obtaining --

A. There was no other trichlorophenol on the market except small laboratory quantities.

Q. So Metro-Atlantic was unable, as a result of Hooker's contract, to obtain TCP from Hooker.

A. That's right.

Q. And in addition to Diamond Alkali, were there a number of companies making trichlorophenol in the mid-60s?

A. Yes. Many.

Q. And could you identify some of those companies.

A. Dow, Monsanto, Hercules, Thompson Chemical Company, Hooker. They all made, as far as I'm aware, trichlorophenoxy acetic acid. Dow itself sold the sodium salt of trichlorophenol and trichlorophenol as a trade name called Dowicide, and Dowicide was used in various

formulations, the composition of which I have no knowledge, as institutional cleansing agents, purifying agents, germicides, what have you. And they were made by the millions of pounds.

MR. BINDER: Okay. This might be -- we've been here for about an hour and a half. This might be a convenient time to take a break, stretch your legs and bring you back here in about five minutes or so.

THE WITNESS: I'm comfortable.

MR. PORTER: I could use a break.

(Break taken at 10:34 a.m. until 10:57 a.m.)

MR. BINDER: Q. Mr. Cleary, you identified Sterling Winthrop and Kalo as purchasers of hexachlorophene from Metro-Atlantic.

A. Yeah.

Q. Do you recall the names of any others -- purchasers?

A. No, there were no others. Sterling would have taken every pound we could make.

Q. Okay. Now, you also mentioned -- let me withdraw the question.

Do you recall the approximate length of the time that Metro-Atlantic was making hexachlorophene at its plant?

A. Only vaguely. Probably -- less than a year.

Q. And this was a plant that was in the vicinity of Providence, Rhode Island?

A. Oh, yes. It was in the community called Centredale.

Q. And you visited that site.

A. Yes, I did.

Q. Okay. Do you recall where on the plant the building was located where the hexachlorophene was manufactured?

A. Fairly precisely, yes.

Q. Would it be helpful if I were to show you a map of the site?

A. I have those maps. I've looked at them all very carefully, yes.

Q. Okay. I have -- I'm going to put before the witness a Sanborn Library Insurance Map, a counterpart of which has been used in a number of other depositions in this case. This bears production No. SBSF 6816.

And I'm going to ask the witness if he can mark the location of the building where he saw the hexachlorophene being manufactured at Metro-Atlantic.

A. I don't have this map, but I have similar maps that were produced by IT of Hopkinton for EPA -- or for the State of Rhode Island, rather. I'm getting my. . .

Q. Maybe I could help you a bit with the orientation.

A. Yes. It usually throws me a little bit here.

Q. Okay. I think if we see at the top --

A. Smith Street was Route 44.

Q. On the top we see a section marked, "Metro-Atlantic, Inc., Chemical Manufacturing." And then we see to the -- oh, west of that, the -- that building, the Woonasquatucket River. And then we see to the southwest, a building that's abutting the river.

A. Uh-huh.

MR. PORTER: This one here, you mean?

MR. BINDER: Yes.

THE WITNESS: It was either that or close to it.

MR. BINDER: Q. When you say "that," are you referring to the building abutting the river?

A. Yes.

Q. Okay.

A. I can't be sure, but it was very close to that, I know. It was right next door to Metro-Atlantic. My recollection is that it actually was between Metro-Atlantic's buildings and the river.

Q. So the record is clear, Mr. Cleary, I'm going to ask if you could mark in red ink an arrow pointing to the building which you said was close to, if not precisely,

where the hexachlorophene was manufactured.

We talked about a building abutting the river.

A. I don't think so. It wasn't located that far away. If these were Metro-Atlantic buildings -- first, let me just review a little bit to orient myself here.

I came on the property off of Smith Street and they had office buildings here (indicating). They had formulation buildings in the middle. And back at this end (indicating), they had their only really chemical operation, which was the manufacture of that meta-nitrobenzene sodium sulfonate I spoke about before that was located right in there (indicating).

But the hexachlorophene building was more like here (indicating).

Q. Away from the other three buildings that you've just described.

A. Separate from.

Q. Separate. Excuse me.

A. Separate from them.

Q. And closer to the river?

A. And closer to the river, yeah. Right about -- I can't write anything with that.

Q. It's a tough pen. Let me just --

A. It was right about there (indicating).

Q. But it was not in the other buildings.

A. No, it was not. It was separate.

MR. PORTER: Not shown on this map, then.

THE WITNESS: No, I don't think so. It could have been anywhere in this space here (indicating), but it was not up there (indicating). It was down in here (indicating) somewhere.

MR. BINDER: Okay. Thank you, Mr. Cleary.

Q. Okay. I guess, in response to my question, you mentioned, once again, the somewhat long chemical name that I forget of the first product that you helped Metro-Atlantic broker.

A. It was Treflan, or trifluralin, for Lilly.

Q. Wasn't there a product before that that went to Winthrop?

A. Well, we went over that. They were already in manufacture of that. And I sought them out, knowing that they made it and proposed to them that we sell some of their material to a customer we already had.

Q. Okay. So you worked with Metro-Atlantic with three products.

A. Yes.

Q. That antibleeding agent that we spoke about earlier that they were already manufacturing.

A. Yes.

Q. The Treflan you just mentioned.

A. Yes.

Q. And the --

A. Hexachlorophene.

Q. Hexachlorophene.

A. Yes.

Q. Did you work with Metro-Atlantic in connection with its manufacture of any other products?

A. No.

Q. Okay. Now, you mentioned -- let me ask you a couple more details, if I could, about the hexachlorophene process.

A. Sure.

Q. Do you happen to recall the particular acid catalyst that was used in that process?

A. Yes. Sulfuric acid.

Q. And do you recall the specific sulfonic acid that was used in the process?

A. None. That was just window dressing in the patent.

Q. And there was also -- was PCE used in the process?

A. PCE?

Q. Perc, PCE, perchloroethylene.

A. Oh, yes. Yeah. Yes, we used that.

Q. Forgive me for using the shorthand.

A. That's all right. We called it "perc."

Q. Do you happen to know the suppliers from whom Metro-Atlantic obtained the perc or the --

A. No. It was a commonly available chemical from -- usually from distributors in drums from anywhere.

Q. And do you know whether Metro-Atlantic stored any of the chemicals used in the hexachlorophene process in tanks?

A. No, they did not. The crude trichlorophenol was supplied in tank trucks, which were not all that large in volume, probably 5,000 gallons at the most. Maybe less than that. And that perhaps was stored in some intermediate place rather than keep it on the premises in the truck, but I don't recall.

Q. You don't know where the TCP was stored.

A. No.

Q. Okay. Now, as a result of Metro-Atlantic selling the hexachlorophene to Sterling Winthrop, I assume that you -- Centerchem obtained a commission for its efforts.

A. Yes.

Q. And it also obtained a commission on sales to Kalo?

A. Yes.

Q. Okay. Would Centerchem still have any records left that go back that far that might tell us for how long

that --

A. I doubt very much because it happened when I first became aware of interest in this case, which is approximately three years ago, I spoke with someone there with that very question. And there is nothing left there.

Q. Now, you also mentioned that Metro-Atlantic was working with Lilly on a product known as Treflan?

A. That's right.

Q. And were you familiar with the process by which Treflan was manufactured?

A. I developed it.

Q. Could you describe that process to us, please.

A. It started with a chemical called trifluoromethylchlorobenzene, which was made, again, by Hooker, and it was purchased by Lilly. It was shipped by Lilly or arranged to have been shipped by Lilly directly to Metro-Atlantic. It was then nitrated in two steps, one of which was very easy and one of which was very difficult.

And the dinitrated product was reacted with dipropylamine, which was also shipped by Lilly directly to Metro-Atlantic and which had many -- not many, but a few producers. Who they were, I'm not sure.

At that time or during that time, a person from Lilly came to these premises and supervised the

formulation of the final product, which involved confidential solvents and emulsifiers, which we never knew about as far as their identity was concerned. So they personally participated in the final production of the goods that they sold.

Q. "They" being Lilly.

A. I beg your pardon?

Q. "They" being Lilly.

A. "They" being Lilly, yes. In fact, a person also now deceased by the name of Robert Dille, D-i-l-l-e.

Q. And how frequently did the Eli Lilly people visit the site while Metro-Atlantic was making the --

A. When it was appropriate. You got to a point in the production when his services and the materials that were confidential to him were timely to arrive there in terms of what was ready for him, which was not continuously, but from batch to batch, you might say. I don't think he was present there more than three or four times, at most.

Q. Okay. And what is the product -- could you describe the process of denitration?

A. Of the nitration?

Q. Was it denitration?

A. Dinitration.

Q. Dinitration. Excuse me.

A. Yes. First the raw material from Hooker, which was trifluoromethylchlorobenzene, was nitrated under what then would be called extremely mild conditions, where a mixture of sulfuric and nitric acid -- the nitric acid being more or less exactly equivalent to what was needed to nitrate -- of the first nitration of that, leaving some sulfuric acid as a by-product.

The second nitration was much more difficult. It involved an excess of nitric acid and a high temperature, around 120, think. 120 degrees centigrade. And then it was -- it was a heterogeneous reaction mixture. So that the product separated from the reaction mixture in a discrete layer, which was separated as a liquid. And that liquid was then reacted with the dipropylamine with the elimination of sodium chloride, actually, because the reaction was neutralized -- as the hydrochloric acid was eliminated, it was neutralized with sodium chloride -- sodium hydroxide to form sodium chloride.

Q. Do you have any knowledge of some of the constituents of the confidential solvents that were used making the Treflan?

A. No, none.

Q. Not any of the constituency?

A. Not a -- not a trace.

Q. Is that also true for the emulsifiers?

A. Yes.

Q. When Metro-Atlantic was manufacturing the Treflan for Eli Lilly, were any -- did you see -- were any by-products generated?

A. Essentially not, because both of those reactions -- all three of those reactions were virtually quantitative. Meaning that there were no by-products or leftovers or residues of organic materials.

Q. Does that mean no wastes were generated, either?

A. Acid waste.

Q. Acid waste. And do you know what happened with the acid waste?

A. No.

Q. Am I correct that both the Treflan and the hexachlorophene were made in the same building?

A. Yes.

Q. And they were made at different times.

A. Oh, very different.

Q. First the Treflan and then the hexachlorophene.

A. Yeah. With a long interlude in between. Several months, at least.

Q. And do you happen to recall the -- the building, was that a two-story building?

A. Well, buildings like that normally are constructed on a mezzanine basis. They have two stories,

in effect, but they're open. Equipment is arrayed around the mezzanine of the main floor to make use of gravity, in some cases, for flowing from one vessel to another, and so that someone on the main floor can visually observe almost everything in the plant from one point where he stands on the floor. So, in effect, two stories, yeah. Two operating levels.

Q. Do you recall whether there were any -- what the floor was made of in those buildings?

A. The floor?

Q. The floor, yes.

A. Cement.

Q. Do you know whether there were any drains in the floor?

A. I don't remember.

Q. Did you ever witness the cleaning of any of the vessels in which either the Treflan or the hexachlorophene was made?

A. No.

Q. Now, at Metro-Atlantic, you had dealings with Joseph Buonanno?

A. Yes.

Q. And George Huse?

A. Yes.

Q. Do you recall having dealings with anybody else

at Metro-Atlantic?

A. No. I knew some of them, but I didn't deal with them in any way.

Q. Who were some of the other people at Metro-Atlantic that you knew of by name?

A. I knew Hug Bonino, who was Buonanno's partner. I knew Joe Buonanno's brother, Bernie. I casually knew a couple of the operators in the plant. Very casually. I don't even remember their names.

Q. Okay. These operators you casually knew, would they include the people who worked in the building where the hexachlorophene and Treflan was made?

A. I suppose so. I mean, I walked past them from time to time, but that's about the size of it.

Q. When the hexachlorophene was being made, did you see, for instance, George Huse walking about the plant floor supervising the activities?

A. I must have, yes.

Q. Okay. At some point, I think you said about three years ago, you became aware of -- about an EPA proceeding regarding the condition of the Centredale site?

A. I first became aware of it by way of Vincent Buonanno, who asked me to have telephone conversations with his attorneys and with his environmental consultant, a person in Washington whose name I forget. The man in --

the legal person was one Deming Sherman from the firm. . .

Q. Does Edwards and Angell ring a bell?

A. Something and Angell.

Q. Edwards and Angell?

A. Edwards and Angell, yeah.

Q. Okay. What subjects did you discuss with them?

A. Pretty much what I've been discussing with you, I guess.

Q. Okay. And then after you learned about the -- after you had a discussion with the -- Mr. Buonanno and his attorney, who did you next have any discussions with about the condition of the site?

A. Well, what happened in my discussion with Vincent, he arranged, via Deming Sherman, to send me a large number of maps which had been prepared by IT at the instigation of the State of Rhode Island listing analyses of various substances that had been found on that property. And asking me if I could identify the source of any of them, which I couldn't and so advised both his attorney and Vincent.

And that pretty much was -- I wrote Vincent a couple of little notes, which I have here if you'd like to see them, giving my impression of what I saw, what I saw in the maps.

Shall I show them to you?

Q. Sure. I'd be happy to see them.

A. I have the maps here, too. I don't know whether you've seen these particular maps.

And then, of course, that was followed very quickly by a contact from Lilly's lawyer, who wanted me to sign their affidavit. Which I did after having made some corrections in it.

Q. Okay. If you're able to find the letters to Mr. Buonanno, that would be great and I will get back to you about --

A. I know I have them here. They were faxes, actually. Here's one (indicating).

MR. PORTER: Mr. Binder, I should have asked this question earlier maybe, but this deposition is just to get information; you have neither the intent nor even the remote expectation that Mr. Cleary is going to be a party to this case.

MR. BINDER: No. This to is to get information for this lawsuit before us.

MR. PORTER: All right.

THE WITNESS: Those simply indicate that I knew nothing whatsoever about all of the contaminants found on that property.

MR. BINDER: Okay. Just so -- Mr. Cleary has been good enough to give us two letters.

Q. These are the two letters that you sent to Mr. Buonanno?

A. That's right.

Q. Could I ask that these be marked as the next numbers in sequence, please.

(Plaintiff's Exhibit Nos. 9 and 10 were marked for identification.)

MR. BINDER: Q. Just to tie up a loose end, Mr. Cleary. I think the next thing you heard after speaking with Mr. Buonanno is you ultimately signed an affidavit that was submitted by counsel for Lilly.

A. Yes.

Q. And that you then made some changes to and then signed when it was correct.

A. Yes.

Q. Let me show you a document bearing production numbers SBSF 12922 through 12924, which I'm going to ask the reporter to mark as the next exhibit.

(Plaintiff's Exhibit No. 11 was marked for identification.)

MR. BINDER: Q. And my question, Mr. Cleary: Is Exhibit 11 the affidavit that you signed?

A. Well, it has my name on it.

Q. It has your name and it has your signature?

A. Yes.

Q. And the information in there is correct to the best of your knowledge?

A. Yes.

Q. Okay. Now after you had the discussions with Mr. Buonanno and his lawyer and Mr. -- the lawyer for Lilly, did you have some discussions about this Centredale site with anybody from the EPA?

A. Yes. A Ms. Ann Gardner, who described herself as a paralegal.

Q. And you've brought with you in response to the subpoena copies of some correspondence you had with Ms. Gardner. Is that correct?

A. We had a -- the first thing that happened was that we had a rather lengthy phone conversation, which she made clear to me that she was going to make the basis of a statement by myself.

And subsequent to that, she sent her resume of that conversation intended to be -- or to reflect my statement. And I sent it back to her with corrections and additional comments. And she told me that she would use that material to conclude some sort of a statement from me.

And when this notice of the deposition came up, I phoned her and asked her if she had a revised copy of such a letter that would have reflected my subsequent

corrections and comments. And she said she hadn't prepared it yet but that she would do so in due course. And those notes I sent to you are a composite of her -- my original conversation with her, my corrections noted where they belonged, and additional comments that I wanted to put into such a letter.

Q. Now, let me try to show you some of these documents so that we can identify the documents you've spoken about.

I'm going to ask the reporter to mark as the next exhibit a three-page memorandum dated November 26, 2002.

(Plaintiff's Exhibit No. 12 was marked for identification.)

MR. BINDER: Q. Now, Mr. Cleary, is Exhibit 12 the memorandum you received from the -- Ms. Gardner of the EPA which you've just mentioned?

A. Yes.

Q. Okay. Thank you.

I'm going to ask the reporter to mark as the next two exhibits copies of letters from Ms. Gardner to Mr. Cleary; the first dated November 26, 2002, the second dated January 14, 2003.

(Plaintiff's Exhibit Nos. 13 and 14 were marked for identification.)

MR. BINDER: Q. Okay. Now, is Exhibit 13 the

letter from Ms. Gardner to you in which she forwarded to you her draft memorandum that's been marked as Exhibit 12?

A. Yes.

Q. Exhibit 14 is also a letter to you from Ms. Gardner. And in this one, she says she's enclosing a copy of her draft memo to the file concerning her telephone conversation with you. Did she enclose the same document, Exhibit 12, with both of those letters?

A. What happened was that when I sent back to her her letter and my corrections, I neglected to keep a copy of her letter. And I told her that, and she said she would send me back a copy of it.

Q. Okay. So you would have gotten -- probably received a copy of Exhibit 12 twice; once --

A. Yeah.

Q. -- with Exhibit 13 and once with Exhibit 14.

A. Right.

Q. Now, you mentioned your corrections to Ms. Gardener's memo. I'm going to show you a handwritten letter dated 12/2/02, which I'm going to ask the reporter to mark as Exhibit 15.

(Plaintiff's Exhibit No. 15 was marked for identification.)

MR. BINDER: Q. And my question to you is whether Exhibit 15 consists of your corrections to

Ms. Gardener's memorandum?

A. Yes, they do.

Q. So if I understand correctly, Mr. Cleary, in order to have an accurate statement of what you discussed with Ms. Gardner, we would take Exhibit 12, incorporate the instances where you crossed out a word and replaced it with another word.

A. Yes.

Q. And then we would place the "1" from Exhibit 15 next to where it says "1" on Exhibit 12.

A. Yes.

Q. We would place the "2" on Exhibit 15 where it's marked "2" on Exhibit 12.

A. Yes.

Q. And we would place the "A" on Exhibit 15 where there's an "A" on Exhibit 12.

A. Right.

Q. Now, in addition to the exhibits we've spoken about today, you also brought some other documents in response to the subpoena. Is that correct?

A. You mean in addition to what you have?

Q. Yes -- no, in addition to what we've already marked as exhibits.

A. Well, what I have here mainly, besides the communication with Ms. Gardner and with Vincent Buonanno,

are the maps that were supplied to me by Vincent Buonanno's attorney which depict the locations and nature of the so-called contaminants that were found on that property.

Q. Okay. Have you brought those with you today?

A. Yes, I have them.

Q. Could we take a look at them.

A. Sure.

These -- I've separated out the ones, I think, which have some relationship to dioxin. These are dioxin-marked maps. And these are maps that are marked with many other things, including what are called volatile organic compounds, semi-volatile organic compounds, PCBs, and heavy metals.

Q. Okay. And these maps are maps from a -- made by a company known as IT Corporation?

A. Yes.

MR. BINDER: I'm going to ask the reporter to mark as the next exhibit in sequence what the witness referred to as the maps from IT Corporation that were dioxin related.

THE WITNESS: They were commissioned by the State of Rhode Island, as I understand it.

(Plaintiff's Exhibit No. 16 was marked for identification.)

MR. BINDER: And I'm going to ask the reporter to mark as Exhibit 17 what the witness described as the maps from IT that were not dioxin related.

(Plaintiff's Exhibit No. 17 was marked for identification.)

MR. BINDER: Q. Now, I know that in response to the subpoena that we arranged to have served on you today, you've produced some other documents, including a copy of an affidavit and a copy of several patents.

I'm going to ask the witness to mark -- excuse me, the reporter to mark as the next group exhibit an affidavit and series of patents and ask whether these are documents you brought today -- actually, brought last evening in response to the subpoena?

A. Is that a question to me?

Q. Yes, it is.

A. Yes, it is.

(Plaintiff's Exhibit No. 18 was marked for identification.)

MR. BINDER: Q. Okay. Now, Mr. Cleary, after you learned about the condition of the Centredale site, did you gather together information about dioxin and other contaminants?

A. Well, I did not learn about the condition of the Centredale site until my initial conversation with Vincent

Buonanno.

Q. Sure.

A. After which, I was sent those maps by his attorneys, and I was requested by Vincent to use my best recollection to try to identify where these various substances might have come from. And my correspondence with him, which also included a couple of telephone calls, were simply that I did not know where they could have come from.

The dioxin, I could by that time have suspected where it came from. All of the other items I had not the slightest idea where they might have come from.

Q. Thank you. I guess let me ask my question I had in mind a little bit differently. In response to this subpoena, you have brought copies of two pages from the Merck's -- Merck Index on which you've written the word "dioxin."

I'm going to show you these as the next exhibit.

(Plaintiff's Exhibit No. 19 was marked for identification.)

MR. BINDER: Q. And is this handwriting on Exhibit 19 yours?

A. Yes.

Q. Look at both pages; it is a two-page document.

A. Yes.

Q. Okay. And did you gather this material that's Exhibit 19 at some point after you had the conversation with Mr. Buonanno's attorney?

A. No. I've had this information for years. It's been in the Merck Index, of which I have had a copy for years.

Q. Okay. I guess my question is: Did you find these particular pages that are Exhibit 19 after you spoke to Mr. Buonanno's lawyer?

A. Well, I can't answer that yes or no.

Q. Okay.

A. It was simply a matter of trying to instruct the related parties, to some extent, as to what the nature of these various chemicals is.

Q. Okay. That was the purpose --

A. And their relationship --

Q. -- of Exhibit 19.

A. And their relationship to each other. And that was my intention, also, in sending them to you.

Q. Okay. That was your intention in creating Exhibit 19.

A. Yes.

MR. McCLOSKEY: Objection.

MR. BINDER: Q. Was that also your intention in preparing Exhibit 19?

A. I don't follow you.

Q. Okay. In response to the previous question, you said that you gathered together materials to explain the different --

A. My assumption, right or wrong, had been that anyone I was going to discuss these matters with had only a fragmentary, and perhaps inaccurate, conception of what these chemicals look like and what their relationship is to one another. And my copying out those pieces from the Merck Index, which I had for years, was intended to elucidate the connection between trichlorophenol, dioxin, 2,4,5-T, hexachlorophene, trichlorophenol, 2,4,5-, et cetera.

Q. Sure. And you were doing that in response to inquiries about -- that lawyers had made about the Centredale site.

A. Yes.

Q. I'm going do show you another group of documents consisting of --

Off the record for a second.

(Off the record.)

(Break taken at 11:44 a.m. until 12:08 p.m.)

(Plaintiff's Exhibit Nos. 20 and 21 were marked for identification.)

MR. BINDER: Q. Okay, Mr. Cleary. I'm going to

show you what's been marked as Exhibit 20. It's a page from the document you produced entitled, "U.S. Pharmacopeia, The Standard of Quality."

Could you identify what that is, please.

A. Well, yeah. I put this in here so you would know that the U.S. Pharmacopeia, which is abbreviated as USP, is an actual compendium which is recognized all over the industry as a collection of acceptable standards in the -- particularly in the drug business.

Where it -- what sort of elevated niche it occupies today, I don't know. But in the absence of any other specifications for a purchased drug -- quote, drug or chemical material, it was often specified as "USP quality." And anytime something new came along that was of more than average commercial interest, the USP soon enough wrote a page of acceptable specifications for that product.

And in due time, I'm not exactly sure exactly when, hexachlorophene appeared in the USP and it became a standard of buying and selling the article. It's a fact, however, that there were times when, possibly due to the pressure of the manufacturer, the Pharmacopeia specifications were a little on the loose side in practical terms. But. . .

Q. So if I'm correct, Exhibit 20 is a copy of --

A. This is a copy of a magazine that I got from somewhere recently.

Q. That's a recent copy, not the one that was in effect in the 1960s, when the --

A. No. This copy is no more than a month old.

Q. Okay.

A. From the press.

Q. When you testified earlier that Metro-Atlantic made the hexachlorophene in accordance with the U.S. Pharmacopeia specified by Sterling Winthrop, you were referring to an earlier edition. Right?

A. As a matter of fact, it exceeded the specifications contained in the USP at the time. This is a page out of a journal which is simply called Pharma. It's a journal that represents all kinds of companies who have connection with the pharmaceutical business.

Q. Thank you.

A. And I just brought this along to show that the USP is a real thing, not a mythical organization.

Q. Okay. That's what I was trying to find out, just to be sure. This is current, not what was in effect in the '60s.

A. It's current. The journal was founded in the 1820s and it still is an annual publication which is used, I'm sure, as a basis for specifications for many, many

items.

Q. Okay. Thank you. I've got a set of handwritten notes you provided in response to the subpoena which the reporter has marked as Exhibit 21.

Are these a set of notes that you made?

A. Yes.

Q. And what was the purpose of your making those notes?

A. The purpose was, again, to elucidate the relationship between trichlorophenol, 2,4,5-T, how it's possible under excessive conditions to have dioxin result from the universal method of making trichlorophenol. And it's intended to be educational.

Q. Okay. Thank you.

I'm going to ask the reporter to mark as the next exhibit, 22, a group of six pages that the witness produced in response to the subpoena.

(Plaintiff's Exhibit No. 22 was marked for identification.)

MR. BINDER: Q. Mr. Cleary, I'm going to give you Exhibit 22 and ask you to take a look at it and to confirm that these are documents you produced in response to the subpoena and that the handwritten notations on the documents in this exhibit are, in fact, yours.

A. Well, these are copies of pages from some of

the -- you understand, my --

Q. Sure.

A. -- my interest in this whole field has declined pretty much over the last several years and I no longer get annual editions of many publications and catalogs that I used to get routinely.

This one is from the so-called Pesticide Dictionary, which is an annual publication produced somewhere in the midwest. And it lists every substance that has an agricultural application, every chemical substance.

And this is just to indicate that hexachlorophene itself not only had an agricultural use, but that it was among items which were classified as having USP quality. That's why I underlined the expression "USP." It's from a journal called the Pesticide Dictionary, Farm Chemicals Handbook.

This is from an annual publication which, for short, is called "The Green Book." It's published every year. It contains a list of every chemical that is sold in the trade -- every one that the publishers of the magazine know about, anyway -- and it lists hexachlorophene. And this is from 1997, I think.

And it not only lists hexachlorophene, but it lists hexachlorophene, dioxin free. See, after dioxin

became a bone of contention with hexachlorophene users, certain producers went out of their way to make trichlorophenol by a way which I -- which I developed myself, actually, eventually, that is totally dioxin free, and the chemistry of which is such that it does not allow for any production of dioxin during the preparation of the hexachlorophene.

And this -- I might mention that the cost of hexachlorophene, which was merely about two dollars and a half a kilo when Metro-Atlantic was making it, when last checked five years ago, was $80 a kilo. Which shows you that somebody is making a handsome profit on it.

Q. Okay. I guess my question is a little simpler. I just want to confirm that these are documents you provided to us and that the writing on them is yours.

A. Yes. Yes, they are.

Q. Thank you. Just to clarify one thing. This dioxin-free hexachlorophene is something much more recent than the '60s, isn't it?

A. Oh, yes. I would say it's been available for 15 years or less.

Q. Thank you.

I'm going to ask the reporter to mark another group of documents that you were good enough to bring to us. And can you just also confirm that this Exhibit 23

also consists of pages with your handwriting that you were good enough to provide after we gave you the subpoena.

(Plaintiff's Exhibit No. 23 was marked for identification.)

THE WITNESS: Yeah, they're all mine. They came from the Merck Index, of which I have a couple of volumes, including the most recent one from which these are taken.

MR. BINDER: Thank you. Okay. I don't have any further questions of you, Mr. Cleary.

Before I say, "Thank you for your time," these other gentleman have a chance, also.

THE WITNESS: Gentlemen, at your convenience.

EXAMINATION

BY MR. ELAM:

Q. Just one simple question, not substantive.

In preparation for your deposition, did you meet with anybody besides your attorney?

A. No. And I rarely met with him except on a social basis.

Q. Okay. That's all I have.

MR. McCLOSKEY: Let's go to Kevin on the phone, and I'll reserve my right to ask some follow-up questions.

Kevin, are you there?

MR. O'CONNOR: Hello?

MR. BINDER: They're passing the baton to you, Kevin. Do you have any questions?

MR. O'CONNOR: Yeah. Hold on a second. I had a very, very difficult time hearing much of what Mr. Clearly said and I'm going to try to be brief here.

EXAMINATION

BY MR. O'CONNOR:

Q. Mr. Cleary, my name is Kevin O'Connor and I represent OneBeacon America Insurance Company.

A. How do you do? I wish I had an arm long enough to reach you.

Q. You were shown a map of the site.

A. Yes.

Q. And if I heard correctly, that was SBSF 061 -- I'm sorry. 06816. Is that correct?

A. Well, I don't know the number, but I know the map you're referring to.

Q. Okay.

Can anyone tell me if that was the 1965 Sanborn map that has been used at other depositions?

MR. BINDER: I believe it was, Kevin. I think that's what the preface of my question said.

MR. O'CONNOR: All right.

Q. Mr. Cleary, when you identified a location that

you thought was the hexachlorophene manufacturing building, did you identify the square building next to the river that's -- next to the word "Woonasquatucket River"?

A. No, I did not.

Q. What building did you identify, if you could reference it to something else on the plan?

A. I don't remember. I could not place that building at all. It may have come after I was acquainted with the property. Many years passed when I did not see the property at all.

Q. Okay. It is fair to say, though, that at some point in time, you became familiar with a building that was constructed and was used for the manufacture of hexachlorophene?

A. Oh, yes.

Q. Did you have any role in the design of that building?

A. No.

Q. Do you know who did?

A. George Huse, mainly.

Q. Okay. Do you know where Mr. Huse is today?

A. He's deceased some 10 or 15 years.

Q. Do you know of anyone else who was involved with the design or the construction of that building?

A. No.

Q. Were you consulted in any way regarding the building specifications necessary to make products in that building?

MR. BINDER: Objection.

THE WITNESS: These matters are extremely commonplace in the trade. There are certain kinds of reactions that you do and certain equipment that is constructed a certain way and certain other kinds of things you do in equipment that's constructed another kind of way.

Most of these implements are standard-issue implements. They are not specially built for any purpose. Some of them can serve very many purposes. And there was nothing about the building, about the equipment that was not totally conventional. It's just a matter of sizing properly. That's the main thing.

MR. O'CONNOR: Q. Are you aware that the Woonasquatucket River and related wetlands have been identified as being contaminated with dioxin?

A. So I'm informed, yes.

Q. Are you aware of any discharge of materials containing dioxin into that river or adjacent wetlands from the --

A. No, I am not. And as a matter of fact, the presence of dioxin, although I can speculate where it came

from and where it was almost certainly present, was not accompanied by other materials that one would expect to be found in the same location. Namely, residual hexachlorophene or residual trichlorophenol.

Q. Are those chemicals that would accumulate in wetland centers?

MR. BINDER: Objection.

THE WITNESS: I'm sorry; I don't follow that question.

MR. O'CONNOR: Q. Well, you're aware that dioxin has been identified as being present in the sediment --

A. Yes, I am.

Q. -- of the river.

A. Yes.

Q. You mentioned two other chemicals.

A. Yes.

Q. What were those chemicals?

A. Yes.

Q. What were those chemicals?

A. They were trichlorophenol, which is the precursor of hexachlorophene, and hexachlorophene itself, some of which might have escaped the premises in some way about which I'm not familiar.

Q. Are those chemicals that would accumulate in

sediments the way dioxin does?

MR. BINDER: Objection.

THE WITNESS: I can't answer that question. I don't know.

MR. O'CONNOR: Q. Do you know what their solubility in water is?

A. They vary. Hexachlorophene itself is practically insoluble in water. Trichlorophenol is more soluble in water. But trichlorophenol itself is a relatively harmless chemical.

Q. Are you aware of what wastewater systems existed in the building that we've talked about at the site?

A. No.

Q. You don't know what the sewage system was?

A. No.

Q. You don't know to where it was piped?

A. No.

Q. And you don't know whether there's been any processed water or processed waste with the waste system?

A. No.

Q. Have you ever seen the construction plans or design documents relating to this building?

A. No.

MR. O'CONNOR: That's all I have. Thank you very much, sir.

THE WITNESS: You're welcome.

MR. McCLOSKEY: Okay. I guess I'm up. I'll keep this brief.

EXAMINATION

BY MR. McCLOSKEY:

Q. I'm Andrew McCloskey. I believe you testified earlier that you were provided with maps that were prepared by IT Corporation --

A. Yes.

Q. -- which described the location of certain contaminants that were found at the Metro-Atlantic site. Do you recall that?

A. Yes.

Q. And then you've also mentioned a few times that you can speculate where the dioxin on the site may have come from.

A. Yes.

Q. What's your speculation in that regard?

MR. BINDER: Objection.

THE WITNESS: Well -- what do these objections --

MR. PORTER: They're for the record. Don't worry about them. The judge will worry about them.

THE WITNESS: Well, the speculation is -- it became more of a fact than a speculation eventually

because it was determined during toxicological studies that were carried out starting mainly in the mid-'70s -- and, again, very largely as a result of the deleterious effects that the application of Agent Orange in Vietnam had had.

Also, you must remember that analytical technology 30, 40 years ago was primitive compared to what it is today. Today you're talking in terms of parts per trillion. In the old days, it was difficult to find anything in terms of a parts per million.

It's known now that the normal production of trichlorophenol by the reaction of sodium hydroxide and methyl alcohol at a certain temperature and pressure will generate dioxin at the rate of about 15 to 25 parts per million based upon the amount of trichlorophenol that is produced.

That was unknown in the days when Dow sold millions of pounds of Dowicide. That was unknown when Dow, Monsanto, Diamond Alkali and others produced and sold millions and millions of pounds of 2,4,5-T that was probably spread on just about every roadway in the United States. And its presence and the chemistry of its formation was not really elucidated until the mid-'70s.

Dioxin itself is a very high-melting organic compound. It has practically no vapor pressure. And it's

said that most of the dioxin that constitutes any suspected hazard is generated by paper bleaching operations, by the general incineration of waste. Much of which, personally, I doubt. But if you read some of the more horrific versions of what dioxin is, does, and where it is, you'll begin to believe that it's on every leaf in creation, that it's falling out of the sky, and so on, but I don't think so.

MR. McCLOSKEY: Q. Well, I appreciate that, but I don't think that you actually answered my initial question.

A. Which is what?

Q. What do you believe is the source of the dioxin on the site?

MR. BINDER: Objection.

THE WITNESS: I just said so. I believe it came in from Diamond Alkali Company, unknown and unsuspected, contained in their crude trichlorophenol solution. And the presence was totally unknown.

MR. McCLOSKEY: Q. I believe you testified that your contact with Metro-Atlantic was when you were employed by Centerchem?

A. That's right.

Q. Okay. Was that the only time that you had contact with Metro-Atlantic?

A. Yes.

Q. How many times were you at the Metro-Atlantic site over the years?

A. Oh, over a period of perhaps four or five years, maybe two or three times a year.

Q. If I understand your testimony correctly, TCP -- or, I'm sorry, dioxin would be included in trace amounts in TCP that was supplied to Metro-Atlantic. Is that correct?

A. I believe that to be the case, yes.

Q. Is dioxin produced in any of the chemical processes where TCP is processed into hexachlorophene? I guess what I'm asking --

A. No, no.

Q. Okay. So there are no additional chemical reactions that would produce additional dioxin?

A. There is no way, physically or chemically, that any other dioxin could have been produced at that location.

Q. I'm not a chemist, so you'll have to forgive me when I ask questions that may seem obvious to you.

A. I'm trying to answer them in a way that would suit a non-chemist.

Q. And you are. I appreciate that.

Do you have any understanding how dioxin that may

have been brought to the Metro-Atlantic site in conjunction with the TCP would have found its way into the river?

MR. BINDER: Objection.

THE WITNESS: No, I don't. As I say, that confuses me because it was -- at least according to the analytical results shown on those maps, it was not accompanied by anything else that could have been associated with the hexachlorophene operation.

MR. McCLOSKEY: Q. You would expect to find other components of hex- --

A. I would have, yes.

MR. BINDER: Objection.

MR. McCLOSKEY: Q. Now, I believe you also testified that, if I understood you correctly, that dioxin concentrations at a level that would cause concern -- and I'm paraphrasing there -- are usually generated by paper bleaching operations and then waste incineration. Did I understand that correctly?

A. That's what one reads in the papers all the time.

Q. What type of waste incineration?

A. Any kind. Dioxin is alleged to occur anytime that refuse or waste or whatever material at all that contains both carbon and chlorine is incinerated.

Q. When was the last time you saw the Metro-Atlantic

site in Centredale?

A. Well, I believe you asked that. After all of the hexachlorophene matter was finished, I maintained a personal friendship with Joe Buonanno for many years. And the general history of the property, as I'm acquainted with, which is only superficially, involved first the merger of Metro-Atlantic with a company called Crown Chemical, which was engaged in a very similar business. That is to say, they sold various agitants, as they were known, to the textile industry. And they merged for the purpose of being acquired.

And my recollection is that they were first acquired by United Shoe Machinery, and the operation was moved to Greenville, South Carolina, and George Huse moved with it. So did Hug Bonino, who was Joe Buonanno's partner in Metro-Atlantic. And Bonino was head of the Crown-Metro operation in Greenville, South Carolina, at a time when I believe that Emhart Industries acquired the property. Or acquired the business.

The rather odd part of the whole picture is that, subsequently, I brought into Crown-Metro in Greenville a very large piece of custom business which was extremely profitable for them. And I believe that during the course of doing that business, which was for a firm known as AmChem in Ambler, Pennsylvania -- it was a weed control

agent that we manufactured for them.

Again, I developed a process for that, helped install it in Greenville, South Carolina. And like all custom work, it finally came to an end. But in the meantime, I'm aware that it was an extremely profitable business for Emhart.

Q. Did that involve the Greenville plant, not --

A. That was strictly in Greenville.

Q. Okay. So after wrapping up the hexachlorophene processes at the Centredale plant, you never had the opportunity to visit that location again?

A. I visited Joe Buonanno there frequently. We played golf together. I introduced him to my son, who was interested in Brown at the time. We were good friends. We stayed good friends. I visited him on his deathbed.

Q. Okay. You never maintained an office at that site, did you?

A. No.

Q. Where was your office during that time period?

A. Manhattan.

Q. And that was maintained at the offices of Centerchem?

A. Yes.

MR. McCLOSKEY: Okay. I appreciate your time. I think that's all that I have. Thank you.

THE WITNESS: You're welcome.

MR. BINDER: I just have a couple of additional questions.

FURTHER EXAMINATION

BY MR. BINDER:

Q. In the process of manufacturing hexachlorophene, as described in your patent and as was followed at Metro-Atlantic, were the trichlorophenols heated?

A. Were they heated?

Q. Yes.

A. Well, they were heated, but they were heated in the company of other substances that were reacting with them during that heating period, and the maximum temperature to which they were heated were not nearly high enough to have caused any side reactions with it.

Q. Okay. And in the course of your different conversations with Joe Buonanno, did you have any discussions with him regarding, you know, the insurance policies that Metro -- that were issued to Metro-Atlantic?

A. No; it was not an issue that was ever mentioned.

MR. BINDER: Okay. I have no further questions.

THE WITNESS: Finito?

MR. BINDER: A couple of other gentleman have to confirm they have nothing further to say. I think,

otherwise, it is.

MR. ELAM: Nothing further.

MR. McCLOSKEY: No, I have nothing further. Thank you.

MR. BINDER: Kevin?

MR. O'CONNOR: No, nothing else.

THE REPORTER: Mr. O'Connor, would you like a copy of the transcript?

MR. O'CONNOR: Yes, I would.

THE REPORTER: Mr. Elam? Mr. McCloskey?

MR. ELAM: Yes, please.

MR. McCLOSKEY: Yes.

THE REPORTER: Thank you.

(The deposition of THOMAS F. CLEARY was concluded at 12:44 p.m.)

CERTIFICATE OF WITNESS

State of California)
) ss.
County of)

I, THOMAS F. CLEARY, hereby declare under penalty of perjury that I have read the foregoing testimony recorded on pages 1 to 97, inclusive, and I certify that:

_____ I have no corrections.

_____ I have corrections, as reflected by letter or handwritten corrections made to the original transcript, and that I now approve my deposition as true and correct.

_____ _____
Date THOMAS F. CLEARY

---oOo---

DISPOSITION OF TRANSCRIPT

I certify that the witness was given the statutory allowable time within which to read and sign the deposition, and that:

_____ The witness failed to appear for such reading and signing.

_____ The witness has waived review/signature on the record.

_____ The witness has reviewed and signed the transcript and has made (no) changes.

_____ A letter of correction has been submitted and is attached to the transcript.

_____ _____
Date LUEL J. SIMSON, CSR No. 4720

REPORTER'S CERTIFICATE

State of California)
) ss.
County of Sonoma)

I, LUEL J. SIMSON, CSR No. 4720, a Certified Shorthand Reporter of the State of California, hereby certify that the witness in the foregoing deposition named to wit: THOMAS F. CLEARY, was by me duly sworn to testify the truth, the whole truth and nothing but the truth in the within-entitled cause;

That the deposition was taken at the time and place therein stated; that the testimony of the said witness was reported by me and was thereafter transcribed into typewriting; that the foregoing is a full, complete and accurate transcription of my shorthand notes taken of the oral proceedings.

I further certify that I am not of counsel or attorney for either or any of the parties in the foregoing deposition and caption named, nor am I in any way interested in the outcome of the cause named in said caption.

IN WITNESS WHEREOF, I have hereunto affixed my signature this 24th day of February, 2003.

LUEL J. SIMSON
Certified Shorthand Reporter
State of California

SIMSON REPORTING
Certified Shorthand Reporters
9546 Ashley Drive
Windsor, California 95492
Telephone: (707) 838-6724
Facsimile: (707) 838-7400

February 24, 2003

Thomas F. Cleary
45451 South Caspar Drive
Mendocino, CA 95460

Re: EMHART INDUSTRIES, INC. v. HOME INSURANCE, et al.
(Deposition taken February 10, 2003)

Dear Mr. Cleary:

The original transcript of your deposition taken in the above-entitled action has been prepared and is available at this office for your review and correction, if necessary. If you are represented by counsel who has a copy of your deposition, you may review that copy and submit to this office by letter any corrections you wish to make.

Unless otherwise directed, the original transcript will be sealed 35 days from the date this notice is sent. If you do not wish to read your deposition transcript, please sign below and return within 35 days from the date this letter was mailed.

You may call to set up an appointment at this office Monday through Friday between the business hours of 8:00 a.m. and 5:00 p.m.

Very truly yours,

Luel J. Simson
CSR No. 4720

_____ _____
Signature Date

UNITED STATES DISTRICT COURT

DISTRICT OF RHODE ISLAND

---oOo---

EMHART INDUSTRIES, INC., Plaintiff,	)	
vs.	)	Civil Action No. 02-053 S
HOME INSURANCE COMPANY, INSURANCE COMPANY OF NORTH AMERICA, LIBERTY MUTUAL INSURANCE COMPANY, NORTH RIVER INSURANCE COMPANY, ONEBEACON AMERICA INSURANCE COMPANY, and UNITED STATES FIRE INSURANCE COMPANY, Defendants.	)	

DEPOSITION OF THOMAS F. CLEARY

Monday, February 10, 2003

Mendocino, California

EXHIBITS

Reported by:
LUEL J. SIMSON, CSR No. 4720

SIMSON REPORTING
Certified Shorthand Reporters
9546 Ashley Drive
Windsor, California 95492
(707) 838-6724

United States Patent Office 2,814,597 Patented Nov. 26, 1957

2,814,597

GERMICIDAL SOAPS COMPOSITION

John M. Wenneis, Port Washington, Thomas F. Cleary, North Bellmore, and Saul Chodroff, Brooklyn, N. Y., assignors to Norda Essential Oil & Chemical Company, New York, N. Y., a corporation of New York

No Drawing. Application March 12, 1953, Serial No. 342,014

8 Claims. (Cl. 252—107)

This invention relates to new chemical compounds which have germicidal activity and which are relatively non-toxic, non-irritating and non-sensitizing, to methods of preparing the same, and to soaps and other detergents containing said compounds in which the desirable germicidal and other properties are retained.

An acceptable germicidal compound must meet a number of desiderata. It must have effective germicidal properties, particularly for the destruction of bacteria under normal conditions of use. If it is to destroy bacteria in contact with the human skin, it must have germicidal activity under these conditions. The germicide must be effective for this purpose in a relatively low concentration in order that it may be economically employed and also utilized in concentrations below that which would impart any adverse effect.

Such a germicide should also be non-toxic, since if it is employed in contact with the human skin it may be absorbed into the body and would be objectionable if it possessed toxic properties. The undesirability of toxic germicides, such as corrosive sublimate, is too well-known to require elaboration.

Furthermore, an acceptable germicide must be relatively non-irritating to the skin. There are many germicides which destroy bacteria and which are not objectionably toxic but which are irritating when used in contact with the skin in that they cause erythema and in extreme cases produce blisters and pustules.

In addition to being non-irritating, an acceptable germicide must be relatively non-sensitizing. A germicide may be unobjectionable, in that it is non-irritative, upon its first use, but upon repeated use the subject may become sensitive to the germicide so that it cannot be reused without adverse results.

The effect of chemical structure on any and all of the above properties is not very well understood, if at all, particularly the effect of structure on irritative properties. Changes in chemical structure which amount to no more than a difference of one chlorine atom on a ring, or in the position of a chlorine atom, markedly affect the results. Compounds so closely related as adjacent homologues similarly give marked differences in results. There is, therefore, no predictability from a consideration of chemical structure of the results obtained in the field of germicidal activity, toxicity, irritative effects, and sensitization.

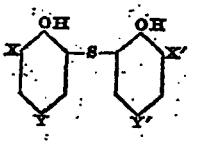
A large number of compounds have been proposed for inclusion with soap to render it germicidal. Since soap is so universally used in cleansing the skin, the inclusion of a satisfactory germicide in soap would be an ideal way of destroying bacteria in contact with the human skin. Many compounds which are recognized as germicides have been proposed for combination with soap, especially various phenolic materials, but because of the depressing action of soap upon the germicidal properties of known germicidal agents, soaps containing such agents do not have germicidal properties. This effect has been demonstrated and is reviewed at some length in U. S. Patent

No. 2,535,077, dated December 26, 1950. In view of this fact, which is now well-recognized in the art, it is not possible to predict, from the germicidal properties of a chemical compound itself, whether a soap containing it would have satisfactory germicidal activity, and would also meet the other requirements discussed above.

Because of the desirability of a germicidal soap, a great deal of research has been done, and at least one germicidal soap has been placed on the market in which the active ingredient is 2,2' - dihydroxy - 3,5,6-3',5',6' - hexachlorodiphenyl methane (also referred to as Hexachlorophene and G-11). Although a soap containing this compound is wanting in some respects, as will be pointed out, it has had wide sales and acceptance as an unusual product in which the germicidal activity is retained in the presence of the soap. In view of the fact that almost twenty-five years of extensive research on a wide variety of compounds preceded the discovery of this particular germicidal soap, it is obvious that the element of predictability is substantially nil and that the discovery of any other compound which could be incorporated in soap with equal or better results would be quite unobvious and unpredictable.

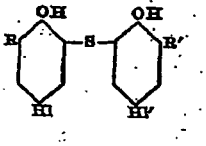
We have discovered, in accordance with our invention, that the following described compounds have germicidal properties and that these properties are retained in soap and that they meet the other desiderata enumerated above, more particularly non-toxicity, non-irritation, and non-sensitization.

These compounds have the following general formula:

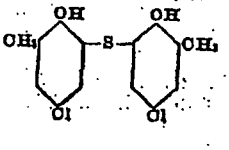


where X and X' are the same or different but are one member selected from the group consisting of (1) a halogen, especially chlorine, bromine and iodine, and preferably chlorine, and (2) an alkyl or cycloalkyl radical having 1 to 8 carbon atoms; and in which Y and Y' are the same or different but are the other members selected from the said group. More particularly, if X and X' are halogen, then Y and Y' are alkyl or cycloalkyl, and if X and X' are alkyl or cycloalkyl, then Y and Y' are halogen. The alkyl or cycloalkyl radical, for instance, may be methyl, isopropyl, octyl, hexyl, cyclohexyl, etc

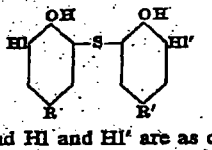
The preferred compounds have the general formula:



in which R and R' are the same or different alkyl or cycloalkyl radicals of 1 to 8 carbon atoms, and HI and HI' are the same or different halogens as defined above, the preferred compound of this type having the following formula:

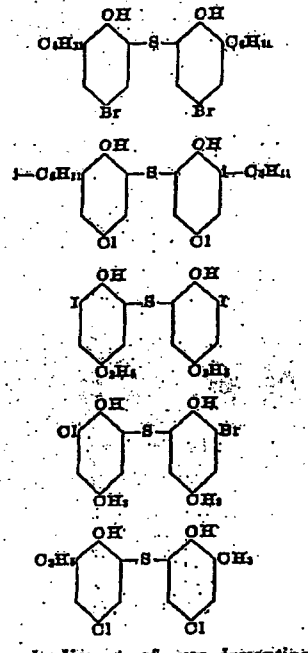


The alternative compounds would have the following formula:



where R and R' and Hl and Hl' are as defined above.

Other compounds falling within the invention include, for example:



A specific embodiment of our invention which we regard at the present time as the best mode that we contemplate for carrying out our invention utilizes the 2-hydroxy-3-methyl-5-chloro phenyl sulfide. This compound has a melting point of about 148–150° C., and is soluble in alcohol, benzene and warm carbon tetrachloride; it is insoluble in carbon disulfide, hexane and water. It is, however, soluble in soap at the normal pH of soap. This compound is selected as illustrative because of simplicity and economic considerations. Compounds in which the hydrocarbon radical has a larger number of carbon atoms may be preferred from a bactericidal and solubility standpoint.

The compounds of the invention may be made by condensing the appropriate halogenated alkyl or cycloalkyl phenol with sulfur dichloride. An inert solvent or reaction medium may be employed which may or may not be a solvent for the final product. The temperature is not particularly critical as long as the reaction takes place at a rate which is controllable. Inasmuch as the reaction proceeds satisfactorily at room temperature, this is preferably employed, since it obviates the need for refrigeration or maintenance of elevated temperatures. A catalyst is not required, nor is extended refluxing essential. The final product is separated from the reaction medium by filtration and can be washed, and if necessary recrystallized to obtain a purer product.

As illustrative of the best mode of practicing the process of preparing the preferred compound of the invention, 28.4 grams of p-chloro-o-cresol and 25 cc. of solvent is placed in a flask and to it is added drop-wise, over a period of about fifteen minutes, 10.2 grams of sulfur dichloride in 10 cc. of the solvent. The mixture is stirred during the addition, which is carried out at room temperature (20–30° C.). The stirring of the mixture is continued until the evolution of hydrogen chloride ceases, which generally requires from thirty minutes to three hours. During this time, the product crystallizes if a solvent is employed in which the reaction product is insoluble. The product is filtered and washed colorless with the solvent generally in an amount of 50–100 cc. The combined filtrates may be stripped of solvent and unreacted sulfur dichloride, preferably in vacuo, to yield oily solids. However, it is difficult to salvage a clean product from such a residue.

The solvent employed in the reaction can influence the yield, ease of handling, and cleanliness of the product. When carbon disulfide is employed as the solvent, a reaction medium commonly used for this type of reaction, the initial yield is 82%, the product having a melting point of 126° C. Upon recrystallization the yield is reduced to 56%, the product having a melting point of 148° C. The high crude yield is not indicative of the final results, since the material salvaged from the second crop of crystals cannot be successfully handled to give a clean product under usual circumstances. For practical purposes, therefore, the yield from carbon disulfide may be considered 56%.

When ethylene dichloride is used, the crude yield is 60%, the product melting at 149° C. When hexane is used as the solvent, the crude yield is 66%, the product melting at 130° C. These crude yields were washed in hexane and not recrystallized. Further losses would be obtained upon recrystallization.

In another variation of the process, the reaction medium may be an ester in which the alcohol and acid radicals have 5 carbon atoms or less, for instance isopropyl acetate. In such solvents, all of the reaction components are soluble, as well as the resulting product, including a large portion of the hydrogen chloride. At the conclusion of the reaction, the product is neutralized with sodium carbonate and stripped of hydrogen chloride. The solvent is evaporated and the resulting product may be recrystallized from any suitable solvent, such as hexane.

The preferred solvent consists of a mixture of ethylene dichloride and hexane, such as, for example, 10 to 50% by volume of ethylene dichloride and 90 to 50% hexane, preferably 22% ethylene dichloride and 72% hexane. The yield from this solvent is 63%, the product having a melting point of 148° C. This initial product is clean and does not need recrystallization. This solvent is preferred because of the higher yield as compared with the yield of recrystallized product when carbon disulfide is used as the solvent and also because of the elimination of recrystallization.

In a modification of this process in which the hydrogen chloride is swept out by bubbling with air until no more hydrogen chloride is evolved, followed by treating the reaction mixture with a slight excess of sodium carbonate solution, the product obtained by filtration and washing with hexane amounted to a yield of 72% without recrystallization.

The use of excess sulfur dichloride does not increase the yield, nor does the use of a chlorine carrier catalyst, such as aluminum chloride, result in advantages; such a catalyst, in fact, reduces the yield and gives a darker product. Refluxing does not affect the yield and leads to a darker product.

The product made by any of the above processes can be decolorized, if desired, by dissolving it in methanol, adding a small amount of activated carbon, such as Darco G–60, at elevated temperature below the boiling point of the methanol, and filtering. The product is precipitated by adding water to the hot solution and cooling gradually with stirring.

In order to demonstrate the effectiveness of the compounds of the present invention as germicides, particularly in soap, a germicidal soap composition was prepared

utilizing as the base a pure white soap of the type conventionally employed for toilet purposes (Ivory), in which was thoroughly incorporated 2% of 2-hydroxy-3-methyl-5-chloro phenyl sulfide. This was tested in comparison with a similar soap containing 2% of Hexachlorophene. These two soaps were tested to determine the skin-degerming efficiency on six subjects each, according to the method of Arthur R. Cade, "An in vivo method for determining the de-germing efficiency of soaps containing Hexachlorophene," Papers on Evaluation of Soaps and Detergents, Special Technical Publication No. 115, published by the American Society for Testing Materials, 1952.

While this test is fully described in the above publication, it may be summarized as follows: Twelve subjects were used for the test. They were divided into two groups of six subjects each, three males and three females in each group, which were used to test each of the above two soaps. Each subject was given two cakes of soap corresponding to his or her group, one for use at home and the other at work. No subject had used any germicidal soap for at least two weeks prior to the test. The test was started on a Monday and ended on the second Friday following, during which time the subjects used their allotted soap when washing their hands. The transient and resident bacterial population on the hands of each subject was determined on the first day prior to starting the use of the experimental soap. The transient and resident bacterial population on the hands of each subject was also determined on the Friday of the first week, after four days' use of the soap, and on the Thursday and Friday of the second week, after nine and ten days' use of the soap.

The details of the method are given in the publication referred to above. Briefly, the method consists in having each subject wash his hands with a bland, non-germicidal, neutral soap, five consecutive times, the first, fourth and fifth times, in separate basins containing 2 liters of lukewarm water. The second and third times the hands were washed under running lukewarm tap water. Bacterial counts were taken on the wash waters in the basins, which represent the first, fourth and fifth washings. The counts on the first washing are considered to be predominantly the transient bacterial population of the skin, whereas the counts on the fourth and fifth washings are considered to be predominantly the resident bacterial population of the skin.

Since the effectiveness of a germicidal soap will be demonstrated primarily by the reduction in the resident bacterial population rather than the transient, the results are expressed as the reduction obtained on the fifth washing. The mean figure is obtained by discarding the two highest and the two lowest values and averaging the remaining two. The mean does not take into consideration a subject who may be out of line with the other subjects. The results are given in the following table:

Reduction in the resident bacterial population (5th washing)

Germicidal agent in soap	Fourth day		Ninth day		Tenth day	
	Average, percent	Mean, percent	Average, percent	Mean, percent	Average, percent	Mean, percent
2-hydroxy-3-methyl-5-chloro phenyl sulfide	72	74	79	81	83	84
Hexachlorophene	68	79	78	81	84	82

It will be obvious that considering both the mean and the average, the soap made in accordance with the invention is as good, and in some instances better than the soap containing Hexachlorophene, which may be considered as the standard reference. As has been explained heretofore, the discovery of Hexachlorophene as a germicide for soap was the result of years of research and is widely accepted as an unusual development in the germicidal soap field. The development of any other soap which equalled this at this stage of the art would be quite unexpected.

The toxicity of the preferred compound of the invention, namely, 2-hydroxy-3-methyl-5-chloro phenyl sulfide, was determined by administering the compound orally to rats. The method employed is the LD_{50} test which may be defined as the amount which, when administered orally as a single dose, will probably kill 50% of the animals to which it is administered. In carrying out the test, normal healthy white albino rats, paired for sex, fasted for 24 hours, were administered various dosages of the compound (dissolved in corn oil) by stomach tube. All animals were observed for at least two weeks following the administration of the dosage, unless death occurred before that time.

The results are given in the following table:

Dose per 100 grams body weight of rat	Number of animals			Percent mortality
	Tested	Living	Dead	
30 milligrams	5	4	1	20
40 milligrams	5	5	0	0
60 milligrams	5	5	0	0
90 milligrams	5	4	1	20
120 milligrams	5	3	2	40
150 milligrams	5	2	3	60
180 milligrams	5	0	5	100

When the results were plotted on semilogarithmic paper, with the percent mortality on the ordinate and the dose on the abscissa (logarithmic scale), the LD_{50} of the compound was found to be approximately 1.3 grams of the compound per kilogram body weight.

As will be obvious to one skilled in the art, this low toxicity, when measured by this standard test, is assurance that the compound is sufficiently safe for use as a germicide in soap.

In order to determine the irritative properties of 2-hydroxy-3-methyl-5-chloro phenyl sulfide, and particularly to compare it with the irritative properties of Hexachlorophene, these two compounds were tested, as well as the sodium salt of both compounds, since the sodium salt probably corresponds to the form of the compound present in soap. The solutions tested were as follows:

Solution A: 0.5% 2-hydroxy-3-methyl-5-chloro phenyl sulfide in aqueous isopropyl alcohol

Solution B: 0.5% Hexachlorophene in aqueous isopropyl alcohol

Solution C: 0.5% sodium salt of 2-hydroxy-3-methyl-5-chloro phenyl sulfide in aqueous isopropyl alcohol

Solution D: 0.5% sodium salt of Hexachlorophene in aqueous isopropyl alcohol

Each solution was tested by the well-known patch test to determine if the compounds would produce contact dermatitis on primary contact. In this test 55 human subjects, 34 females and 21 males, ranging from ten to sixty-three years, were employed. Discs approximately 1 cm. in diameter were cut from white blotting paper and different discs saturated with the four solutions described above. The saturated discs were applied to the flexor surface of either the forearm or the upper arm of each subject, utilizing four patches for each subject. All patches were covered with an Elastopatch. After twenty-four hours of primary contact with the patches, they were removed and the subjects examined. The reactions obtained on every subject following examination were noted, and the severity of reaction was based on an arbitrary scoring system, as follows:

0=No reaction.

1=Slight erythema or discoloration lasting at least four hours after removal of the patch.

2=Rather severe erythema or discoloration lasting at least two days after removal of the patch.

3=Severe circumscribed irritation with blisters or pustules.

The results are given in the following table, which lists the number of subjects in each reaction category:

	Solution A		Solution B		Solution C		Solution D	
Number of 0	12×0= 0		8×0= 0		34×0= 0		25×0= 0	
Number of 1	21×1=21		14×1=14		21×1=21		25×1=25	
Number of 2	21×2=42		32×2=64		0×2= 0		7×2=14	
Number of 3	1×3= 3		8×3= 0		0×3= 0		0×3= 0	
Total	55	66	56	87	55	21	55	39
Average		1.20		1.55		0.38		0.71

From a consideration of the above results, it will be obvious that the compound of the invention, as well as the sodium salt thereof, are much less irritating than the Hexachlorophene. This is particularly true in the case of the sodium salt, the form in which the compound would exist in soap, where the Hexachlorophene is found to be almost again as irritating as the compound of the invention.

In order to determine the sensitizing properties, the irritation test was repeated on each of the subjects by applying patches with the same solution to the same subject, each patch being applied at the site previously used for that particular patch. The patches were again worn for twenty-four hours and the subjects examined in the same manner as described above. The results are given in the following table:

	Solution A		Solution B		Solution C		Solution D	
Number of 0	14×0= 0		7×0= 0		39×0= 0		27×0= 0	
Number of 1	25×1=25		18×1=18		16×1=16		25×1=25	
Number of 2	16×2=32		30×2=60		0×2= 0		3×2= 6	
Number of 3	0×3= 0		0×3= 0		0×3= 0		0×3= 0	
Total	55	57	55	78	55	16	55	31
Average		1.04		1.42		0.29		0.56

From this it will be seen that as compared with Hexachlorophene the compounds of the invention cause less sensitization, and that this is particularly true in the case of the sodium salt of the compound, where the Hexachlorophene is shown to be almost twice as objectionable as the preferred compound of the invention from the standpoint of sensitization.

A low sensitization level is an extremely important aspect of compounds used in germicidal soaps because of the repeated use of such soaps under normal living conditions. It will be obvious that a soap is useless for normal toilet use if it cannot be utilized over long periods of time. To substantiate the non-sensitizing properties of the preferred compound of the invention, the sensitization was determined on white male guinea-pigs by the method described in an article entitled "Methods for the study of irritation and toxicity of substances applied topically to the skin and mucous membranes," John H. Draize, Geoffrey Woodard and Herbert O. Calvery, Journal of Pharmacology and Experimental Therapeutics, vol. 82, No. 4, pages 386–388, December 1944. In this method, ten white male guinea-pigs, weighing 325–450 grams, were used. The hair was removed from the back by close clipping. A 0.1% suspension of the compound in water was injected intracutaneously, using a 26-gauge needle. A total of ten injections were made at random in an area about three to four centimeters square, just below the midline of the back. The first injection was 0.05 ml., while the remaining injections were 0.1 ml. Two weeks after the tenth injection, a test injection of 0.05 ml. of a freshly-prepared suspension was made on the flank, slightly below the sensitizing area. Twenty-four hours later, a reading of the diameter, height and color of the reaction was made and compared with similar readings taken after the first injection.

As a result of this test, it was found that on all ten animals the values for the test readings were no greater than those for the initial readings, and it is concluded that when tested by the above procedure the preferred compound of the invention cannot be considered to be a sensitizer.

The compounds of the invention may be used in soaps, in the so-called non-soap synthetic organic detergents, or in combination with any "organic detergent." This expression is intended to include the soaps which are the salts of higher fatty acids and the so-called non-soap synthetic detergents. All of these compounds are characterized by an organic radical having at least 8 carbon atoms and a group or grouping imparting sufficient hydrophilic, water-solubilizing or water-dispersible properties to give the detergent satisfactory washing properties in water. These organic detergents are to be distinguished from the inorganic detergents, such as the silicates, phosphates, etc., which possess detergent properties but which do not ordinarily have the property of inhibiting the germicidal activity of germicides as do the soaps and synthetic non-soap detergents.

The soap may be any of those commercially utilized in the household or in industry. These are generally the sodium soaps of fatty acids having 12 to 18 carbon atoms, such as lauric, myristic, palmitic, oleic, stearic, etc., or mixtures thereof. The mixtures of fatty acids derived from tallow and coconut oil are illustrative. A portion of the sodium soap may be replaced by potassium soap. As a specific illustrative example, the soap may consist of 75% tallow fatty acids and 25% coconut oil fatty acids saponified with sodium hydroxide. In another specific example, 10% of the sodium hydroxide is replaced by potassium hydroxide. The soap may contain antioxidants, pigments, dyes, perfume, etc., as is conventional.

The non-soap organic detergents may be of the so-called anionic, nonionic or cationic type. Illustrative detergents of this type are described in Industrial and Engineering Chemistry, vol. 35, page 107 et seq. and page 126 et seq. (1943). As specific examples may be mentioned sodium lauryl sulfate (Duponol) and sodium polypropylene benzene sulfonate in which the polypropylene radical contains 10 to 15 carbon atoms (Oronite). Others include the sulfonated monoglycerides of fatty acids, the sodium fatty acid taurides, and methyl taurides such as sodium oleic methyl tauride (Igepon T), coconut fatty alkyl dimethylbenzylammonium chloride (Triton K–60), coconut fatty acid diethanolamide (Ninol), and similar detergents.

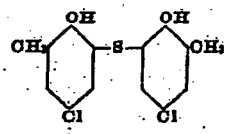
The amount of the compound to be incorporated in the detergent will be controlled somewhat by economic considerations and the extent of the germicidal activity desired in the detergent. Amounts as low as a fraction of 1%, for example 0.25 to 0.5%, show a significant improvement in germicidal action. Larger amounts, however, of the order of 1.5 to 3.0% are preferred, 2.0% appearing to be an optimum. Amounts larger than 3% to 5% are uneconomical, and the use properties are not sufficiently important under the usual circumstances to justify such larger amounts.

The compounds of the invention may be included in soap or detergents in any form, such as in cakes or bars of the type generally sold and used for the toilet, in the all-purpose type, such as the white floating bar, or in powders, liquids, flakes, beads, and similar forms.

The compounds may be incorporated in the soap in any manner. If the soap is a liquid, the compound may simply be dissolved therein; if it is a solid, the compound may be incorporated at any stage of the manufacture, such as in the kettle, the mill, the plodder, the crutcher, etc. so long as uniform distribution is obtained.

We claim:

1. The compound having the following formula:



2. A method of preparing the compound of claim 1 which comprises reacting sulfur dichloride with p-chloro-o-cresol in approximately stoichiometric proportions at a temperature within the range of 20 to 30° C., the sulfur dichloride being added gradually to the p-chloro-o-cresol, both the sulfur dichloride and the p-chloro-o-cresol being dissolved in a reaction medium consisting essentially of from 10 to 50% by volume of ethylene dichloride and from 90 to 50% by volume of hexane, the reaction being carried out with stirring during the addition of the sulfur dichloride until the evaporation of hydrogen chloride ceases.

3. The method of claim 2 in which the reaction is followed by bubbling air through the reaction mixture to strip hydrogen chloride therefrom.

4. The method of claim 2 in which the reaction medium comprises about 22% ethylene dichloride and about 72% hexane.

5. The method of claim 2 in which the reaction medium is about 22% ethylene dichloride and about 72% hexane, and in which the reaction is followed by bubbling air through the reaction mixture to strip hydrogen chloride therefrom.

6. A germicidal detergent composition comprising a fatty acid soap and an amount of the compound of claim 1 to render the composition germicidal.

7. The composition of claim 6 in which the fatty acid soap is a toilet soap in bar form.

8. The composition of claim 7 in which the amount of the compound incorporated is about 2%.

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United States Patent Office 3,456,020 Patented July 15, 1969

3,456,020

PRODUCTION OF 2,2'-METHYLENE BIS(3,4,6-TRICHLOROPHENOL)

Thomas F. Cleary, Summit, N.J., assignor to Centerchem Inc., New York, N.Y., a corporation of New York

No Drawing. Continuation-in-part of application Ser. No. 489,036, Sept. 21, 1965. This application Nov. 28, 1967, Ser. No. 686,290

Int. Cl. C07c 37/00

U.S. Cl. 260—619 3 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to the production of hexachlorophene by a two stage process in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted under the influence of an acid catalyst, after which the reaction product is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid.

RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 489,036, now abandoned, filed Sept. 21, 1965, and having the same title as this application.

THE INVENTION

This invention relates generally to new and useful improvements for the production of 2,2'-methylene bis-(3,4,6-trichlorophenol), commonly called hexachlorophene, and particularly seeks to provide a novel two stage process for producing same.

The known processes for the preparation of hexachlorophene (2,2'-methylene bis(3,4,6-trichlorophenol)) involve the condensation of two mols of 2,4,5-trichlorophenol with one mol of formaldehyde (as Formalin or paraformaldehyde). The usual condensing agent is concentrated sulfuric acid or weak oleum, and the reaction may be carried out in the presence or absence of a solvent which is inert to the reactants and to the condensing agent.

In these processes it is customary to mix all of the reactants (and the solvent, if any) at once and to heat the mixture, with agitation, for a certain time. Conditions such as these are disadvantageous in the production of hexachlorophene in that:

(1) They tend to promote the formation of color bodies which make difficult the purification of the product;

(2) They tend to promote the formation of the by-product 2,4,5-trichlorobenzodioxolane with an attendant loss of yield;

(3) They require, if acceptable yields are to be obtained, extreme care that the 2,4,5-trichlorophenol and formaldehyde be present in exactly the molar ratio 2.00:1.00. Since the composition of Formalin or of formaldehyde is usually imprecise, and since a certain amount of formaldehyde is lost from the reaction mixture by volatilization, this is a difficult requirement to realize in practice.

However, through the use of this invention the above mentioned disadvantages in prior processes have been overcome.

Therefore, an object of this invention is to provide a new method of producing hexachlorophene from previously known source materials which is simpler, more effective and results in higher yields by comparison with prior processes.

Another object of this invention is to provide a process of the character stated in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted

under the influence of an acidic catalyst to form a novel intermediate product, which in turn is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid to produce high yields of pure hexachlorophene.

With these and other objects, the nature of which will be apparent, the invention will be more fully understood by reference to the accompanying detailed description and the appended claims.

In accordance with this invention it has been discovered that:

(1) One mol of 2,4,5-trichlorophenol and one mol of formaldehyde will react, under the influence of acidic catalysts such as benzenesulfonic acid, anhydrous hydrogen, and diluted sulfuric acid, to form quantitatively and exclusively, a compound which has a melting point of 78° C. The compound has a chlorine content 46.5%, occurs in long colorless prisms, and definitely is not 2,4,5-trichlorosaligenin.

(2) The compound formed as in (1) can be condensed with 2,4,5-trichlorophenol, through the agency of chlorosulfonic acid or fluorosulfonic acid, to produce high yields of pure hexachlorophene.

Both of these reactions are surprising. The only hitherto known reaction product of equimolar amounts of 2,4,5-trichlorophenol and formaldehyde is 2,4,5-trichlorosaligenin, which is formed under alkaline conditions and has a melting point of 128° C. 2,4,5-trichlorophenol, which is relatively inert to concentrated sulfuric acid and to oleum, will react readily with chlorosulfonic acid and fluorosulfonic acid to form 2,4,5-trichlorophenol-6-sulfonic acid.

The following examples will illustrate this invention.

Example 1

197.5 grams of 2,4,5-trichlorophenol having a melting point of 66° C. is dissolved in 1000 grams of perchloroethylene and the solution is warmed to 50° C. with agitation. To this solution is added 50 grams of 90° sulfuric acid. 30 grams of paraformaldehyde is added slowly over a period of one hour with sufficient cooling to maintain the temperature between 60° C. and 70° C. The reaction is exothermic. The mixture is stirred for an additional two hours at 70° C. The perchloroethylene solution is then separated from the dilute acid layer. Upon evaporating a small sample to dryness a crystalline product is obtained which has a melting point of 78° C. There is no free formaldehyde remaining either in the dilute acid layer or in the perchloroethylene solution. There is no hexachlorophene present at this point in the reaction mixture, nor any unreacted 2,4,5-trichlorophenol.

The perchloroethylene solution of the product of the reaction between 2,4,5-trichlorophenol and paraformaldehyde is mixed with a solution of 197.5 grams of 2,4,5-trichlorophenol in 1000 grams of perchloroethylene and the mixture is heated with agitation to 75° C. There is then introduced dropwise over a period of three hours 116 grams of chlorosulfonic acid. The addition of chlorosulfonic acid is accompanied by a mild exothermic reaction and by the evolution of HCl. The temperature is maintained at 75° C. throughout the chlorosulfonic acid addition and is then held at 75° C. to 80° C. for an additional two hours. Agitation is stopped, the remaining sulfuric acid layer is allowed to settle and is separated. The hot perchloroethylene solution is stirred with 10 grams of activated charcoal and is filtered. The reaction product, 2,2'-methylene bis(3,4,6-trichlorophenol), crystallizes upon cooling and is separated by filtration. The yield is 310 grams having a melting point of 162° C. Upon concentration of the mother liquors there is obtained an additional 65 grams of product having the same melting point.

Example 2

197.5 grams of 2,4,5-trichlorophenol having a melting point of 62° C. is dissolved in 2000 ml. of chloroform, and the solution is warmed to 50° C. with agitation. Dry hydrogen chloride is bubbled through the solution at a rate of 5 grams per minute, and over a period of one hour, 31.6 grams of 95% paraformaldehyde is added. Hydrogen chloride addition is continued for 30 minutes, and the mixture is then heated to reflux for one hour.

A small sample of the reaction mixture, evaporated to dryness, yields a white crystalline compound, having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

To the reaction mixture is then added a solution of 197.5 grams of 2,4,5-trichlorophenol, having a melting point of 62° C., in 2000 ml. of chloroform. The mixture is heated to 65° C., under a reflux condenser and with good agitation, 100 grams of fluorosulfonic acid is added dropwise, over a period of three hours. Agitation and heating at 65° C. are continued for three hours more, then agitation is stopped, the acid layer is settled and separated. The hot chloroform solution is stirred with 10 grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold chloroform and dried. The yield is 310 grams having a melting point of 164° C. Evaporation of the mother liquor yields an additional 70 grams of product.

Example 3

To 1000 ml. of benzene is added, slowly, 58 grams of chlorosulfonic acid, and the solution is then heated to reflux until all HCl is driven off. There is thus produced a benzene solution containing 79 grams benzenesulfonic acid. To this solution is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is then heated just to the point of reflux, and with good agitation, 85 grams of 37% Formalin is added over two hours, while the water introduced with the Formalin is taken off as an azeotrope with benzene. The condensed benzene is returned to the reaction mixture. Reflux is then continued for one hour, after which 500 ml. of water is added. The mixture stirred 15 minutes at 60° C., and settled. The water layer which contains the benzenesulfonic acid, is separated and discarded.

A small sample of the benzene solution evaporated to dryness, yields a white crystalline product having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

The benzene solution is added to 2000 ml. of perchloroethylene, and the benzene is removed from the mixture by fractional distillation.

To the remaining perchloroethylene solution of the reaction product of 2,4,5-trichlorophenol with Formalin is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is heated to 75° C., and with vigorous agitation is added, over five hours, 116 grams chlorosulfonic acid. Stirring is continued at 75° C. for two hours and the acid layer is then settled and separated. The hot perchloroethylene solution is stirred with ten grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold perchloroethylene and dried. The yield is 280 grams having a melting point of 163° C. Evaporation of the mother liquor yields an additional 85 grams of product.

I claim:

1. In a method for producing hexachlorophene the steps of, supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the pressure of an acid catalyst selected from the group consisting of benzene-sulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid to form a solution of a compound which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%, then adding a solution of 1 mol of 2,4,5-trichlorophenol to the solution containing the reaction product of the preceding step, and effecting condensation therebetween by the addition of a sulfonic acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid to produce pure hexachlorophene.

2. A reatcion product between 2,4,5-trichlorophenol and formaldehyde, having a melting point of 78° C. and a chlorine content of 46.5%, produced by supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the presence of an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid, and separating the solvent solution containing the reaction product from the acid.

3. In a method for producing hexachlorophene the steps of; dissolving a molar equivalent of 2,4,5-trichlorophenol in a solvent selected from the group consisting of perchlorethylene, chloroform and benzene; adding to said solution an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid; then adding a molar equivalent of formaldehyde and maintaining the temperature between about 60° C. and about 70° C. during the exothermic reaction produced as the result of such addition to produce a reaction product which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%; separating the solvent solution from the acid; adding a molar equivalent of 2,4,5-trichlorophenol dissolved in said solvent to said separated solvent solution; effecting condensation between said added molar equivalent of said 2,4,5-trichlorophenol and the reaction product in said separated solvent solution by the addition of an acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid; then removing the solvent solution containing the condensed product and recovering pure hexachlorophene therefrom by cooling and filtering same.

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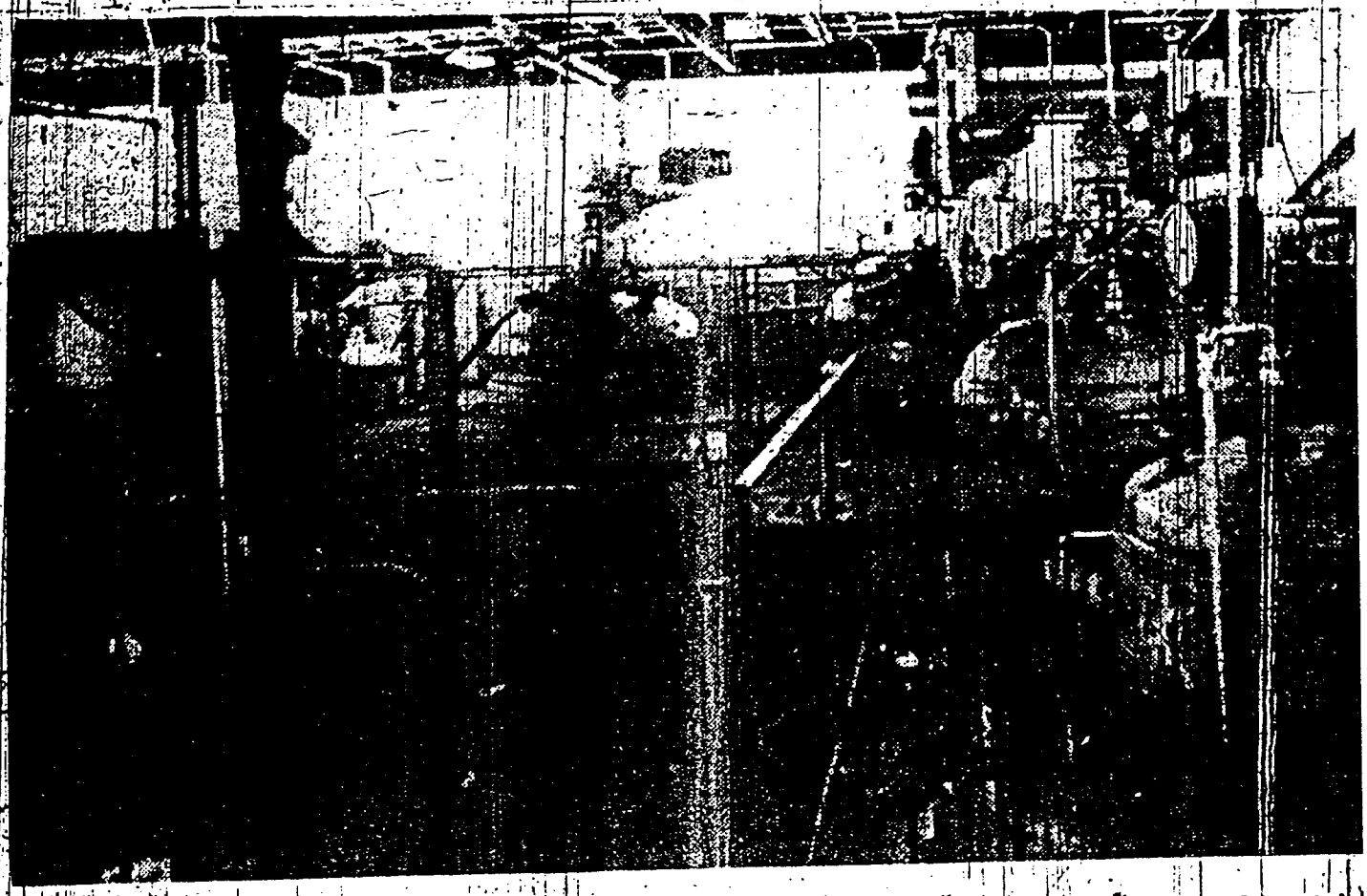
LEON ZITVER, Primary Examiner

N. MORGENSTERN, Assistant Examiner

JS-30-65-B22



Upper level of new hexachlorophene plant at Metro-Atlantic, Inc., Centredale, showing a number of its stain

Pharmaceutical Products Adde

By ARTHUR S. RESEIGH
Journal-Bulletin Business Writer

An entrance into the pharmaceutical field has been achieved by Metro-Atlantic, Inc. of Centredale as a result of a product development program in which it has been active for the past three years.

The chemicals manufacturer, originally a producer of chemical products for the textile industry, has erected a new 2,000 square foot plant for the production of its newest product — hexachlorophene.

The new facility, erected at a reported cost of a quarter of a million dollars, provides Metro-Atlantic with the equipment necessary to produce the new product by means of its newly patented process.

Joseph E. Buonanno, president, said the facility contains enough equipment to produce a complete line of chemical products. It could produce the equivalent of 15 million pounds per year if used for general chemicals production, he said.

The many different pieces of equipment in the new plant, however, are performing single steps in the production of [illegible]

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"We are not setting out to capture the market for this product, but only to acquire a share of it," Mr. Buonanno said. He expressed the opinion that the use of hexachlorophene is on the increase and that another manufacturer will be able to find ample market for his output.

Metro-Atlantic was led into the pharmaceutical chemicals field as a result of a project on which it worked with Eli Lilly Co. of Indianapolis.

The big pharmaceuticals manufacturer needed a large-scale manufacturer for trifluralin, designated in chemical terms as "a,a,a-trifloro-2,6-dinitro-N,N-di-proply-y-toludine," while it was building its own production facility for the prod-

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By ARTHUR S. [illegible]
Journal-Bulletin Business Writer

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The many different pieces of equipment in the new plant, however, are performing single steps in the production of hexachlorophene. The final product, according to George C. Huse, the firm's chemical director, involves a number of highly complicated chemical reactions. The process starts with raw materials and includes such chemical processes as purification, crystallization, recovery of the reactor media, drying, grinding and packaging.

Raw materials are fed from large storage tanks outside the plant. Process equipment includes a dozen different stainless steel, glass-lined low and high temperature reactors—each of them limited to one step of the production cycle.

Product Is Bactericide

Hexachlorophene is a bactericide used in soaps, shaving creams, tooth paste, medical soaps and all kinds of creams and salves for hospital use.

Making the production of hexachlorophene particularly interesting to Metro-Atlantic was the large number of preparations in which it is used and the fact that its production was limited to one manufacturer.

Mr. Huse reports that in one section of a drugstore he visited he counted 34 different products containing hexachlorophene.

"We are not setting out to capture the market for this product, but only to acquire a share of it," Mr. Buonanno said. He expressed the opinion that the use of hexachlorophene is on the increase and that another manufacturer will be able to find ample market for his output.

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The big pharmaceuticals manufacturer needed a large-scale manufacturer for trifluralin, designated in chemical terms as "a,a,a-trifloro-2,6-dinitro-N,N-di-proply-y-toluidine," while it was building its own production facility for the product.

Signed for Production

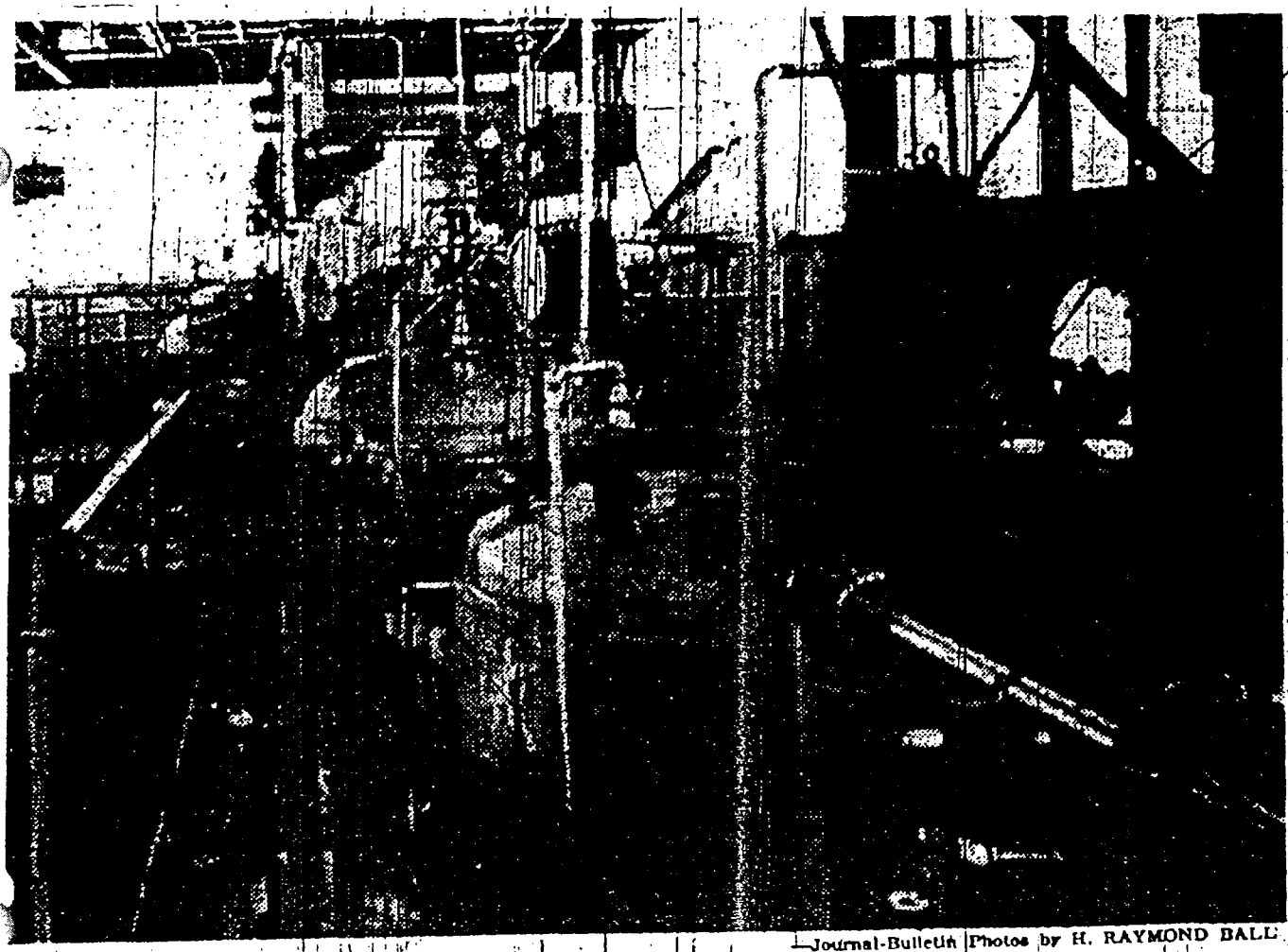
They contacted Metro-Atlantic and set up an arrangement for carrying on the required research and also for producing close to half a million pounds of the product.

The Centredale company worked on the project in collaboration with Eli Lilly Co. for about a year. In that time research was completed, a pilot plant set up and production started. Patents on the product—a post emergence weed killer—were procured and later turned over to the Lilly company.

With the completion of a multi-million-dollar plant, Lilly took over the production of the product. It is designed for specific use on cotton and soybean plantations.

The research and subsequent manufacture of about 500,000 pounds of the product served to interest Metro-Atlantic in the pharmaceutical side of the chemical business.

The facilities used for the trifluralin project became the beginning of the new facility now being used exclusively for the



—Journal-Bulletin Photos by H. RAYMOND BALL

lantic, Inc., Centredale, showing a number of its stainless steel low and high temperature reactors.

l Products Added

CTHUR S. RESEIGH
J-Bulletin Business Writer

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Two other programs are currently in progress at the Centredale plant. When completed, the operation there will be about 25 per cent pharmaceuticals, Mr. Buonanno said. It is our intention, he added, to increase the line of new products

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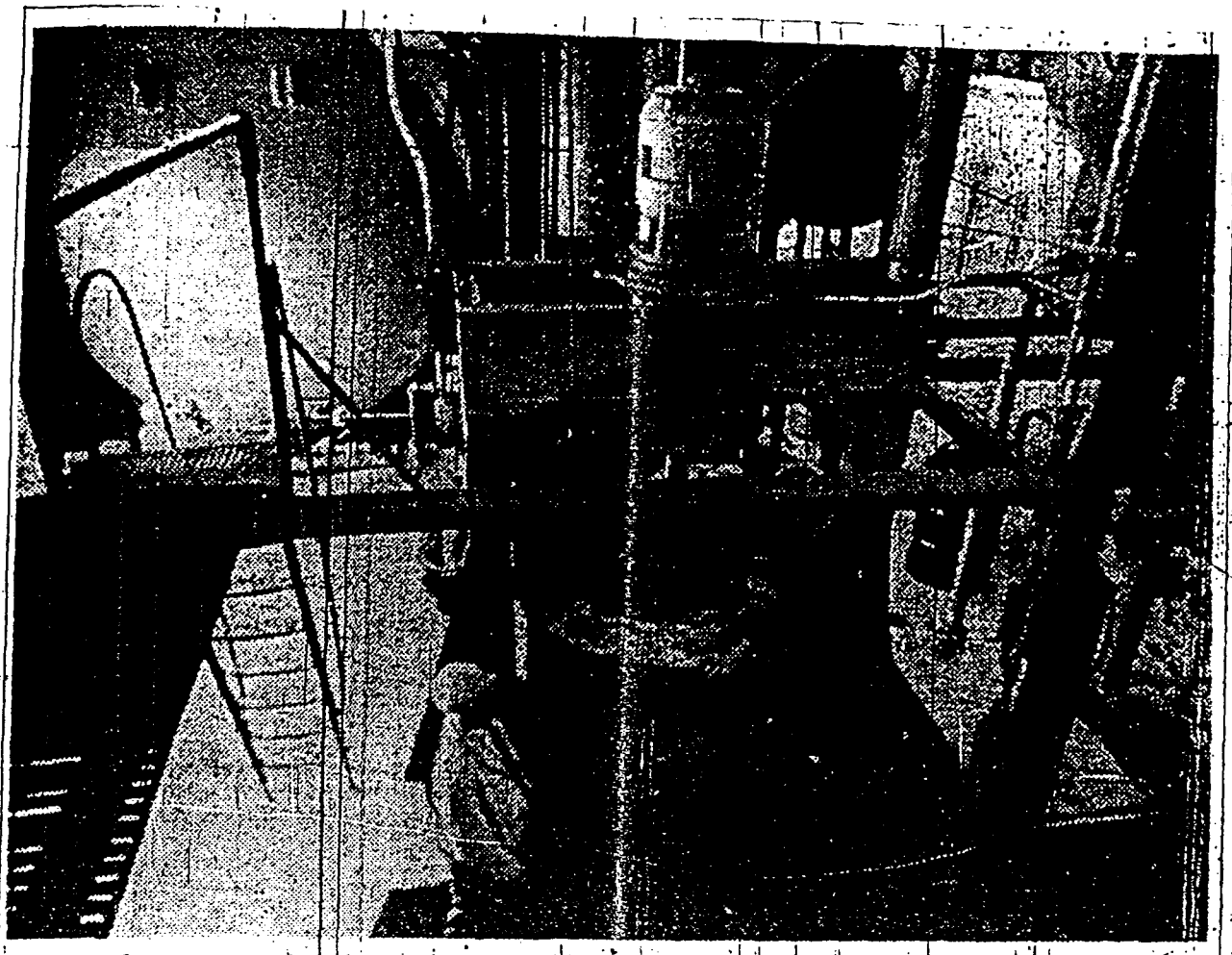

Large perforate centrifuge located in new plant provides company a means of crystal recovery.

CONTINUED from preceding page

Proposed Line of Metro-Atlantic To Be Half Non-Textile Products

until the operation is 50 per cent non-textile.

During the development of non-textile products, the company's volume in its normal textile chemicals has been holding up well, management reported. New products also have been added. These include several textile finishing products, including wash and wear, permanent crease and water repellency items.

The company also is active in chemicals for the metals field. It is making products used for metal finishing and stripping. On some of these, Metro-Atlantic is one of the first two suppliers in the country, Mr. Buonanno said. The line is made in bulk and sold to manufacturers of metal finishes who package and distribute them.

The company also has developed a chrome complex type of water repellent used chiefly in the paper trade. It is expected to be one of Metro's big items.

The company has become one of the first firms of its size to produce mallamine resins—used in textiles to give stiffness and crispness to a fabric.

New Facility Planned

Earlier this month, Metro-Atlantic announced plans to build a $400,000 plant at Don-

about five years, has recently been increased to 50 per cent.

The facility is operated jointly with a Swiss firm and produces die stuffs. The plant supplies the Centerdale operation, the value of the imported product being 50 per cent American and 50 per cent European.

Operated for about 18 years is a Canadian facility, utilized chiefly for selling, but including some textile chemicals manufacture.

Metro-Atlantic additionally is working currently under license arrangements with manufacturing companies for the packaging and distribution of some of the products the firm produces

Military

until the operation is 50 per cent non-textile.

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New Facility Planned

Earlier this month, Metro-Atlantic announced plans to build a $400,000 plant at Donaldson Center, Greenville, S.C., for production of a complete line of textile and paper chemicals. Also planned for this facility, scheduled for completion in the fall, is a line of printing inks for use in the paper trade, a new operation for the company.

Metro also has facilities abroad. One of these is a compounding plant in Brussels, designed to serve the European Common Market. It presently uses chemicals produced in this country, but plans are being considered for the addition of some manufacturing there.

One of its other foreign operations is an interest in the Virgin Islands Chemical Co., St. Croix, Christiansted, V.I. Its interest in the firm, dating back about five years, has recently been increased to 50 per cent.

The facility is operated jointly with a Swiss firm and produces die stuffs. The plant supplies the Centerdale operation, the value of the imported product being 50 per cent American and 50 per cent European.

Operated for about 18 years is a Canadian facility, utilized chiefly for selling, but including some textile chemicals manufacture.

Metro-Atlantic additionally is working currently under license arrangements with manufacturing companies for the packaging and distribution of some of the products the firm produces.

Military Surplus Sales

Inspection may be made and bids submitted up to dates indicated for useable surplus property and scrap for sale at New England military installations. Further information, including location, free sales catalogs and bid instructions, may be obtained from the Defense Surplus Sales Office, Dept. P, P.O. Box 660, Bldg. 115, Newport; telephone 841-3508. Requests should specify sales catalog number for prompt response.

Steel Scrap, June 4—(1 p.m.)—16-S-65-97. Steel scrap unprepared, galvanized (net panels).

Electronics and Aeronautical, June 8—(1 p.m.)—16-S-65-98. Current regulators, magnetron tubes, receivers transmitters, amplifiers, fuel tanks; spinner, stabilizer and strut assemblies, valves, shafts, hydraulic pumps, aircraft heaters, water separators, cylinders, linear actuators, accumulators and lighting fixtures. Original cost: $446,052.

Platinum Tipped Spark Plugs, June 9—(1 p.m.)—16-S-65-99. Platinum tipped spark plugs. Original cost: $11,739.

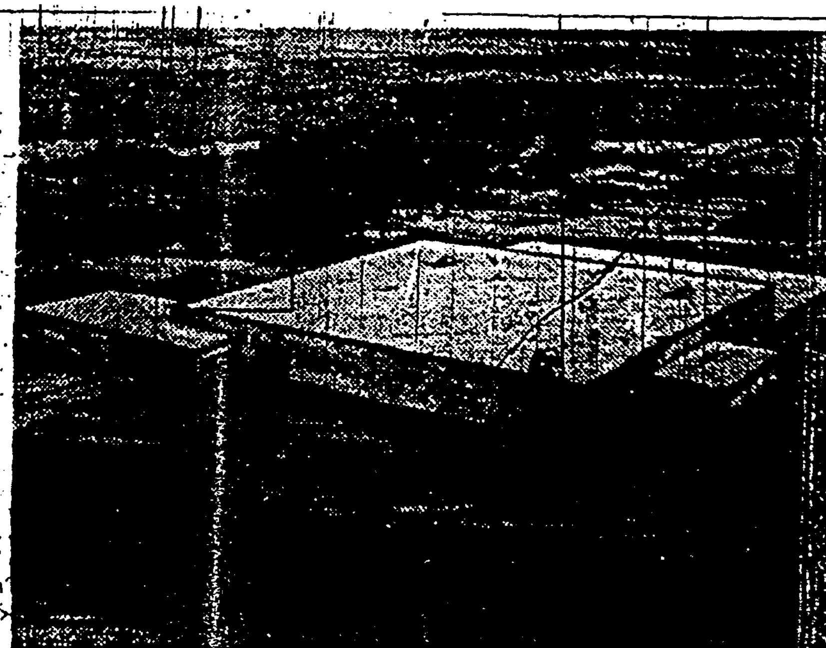
Varied Material, June 10—(1 p.m.)—16-S-65-100. Engine, turret and woodworking lathes, milling machine, wood surfacer; titanium bars, boring bars, cutters, lube oil, sealing compound, leather dressing, clothing and laundry and restaurant equipment. Original cost: $350,022.

NEW CREDIT CARDS

Ft. Lauderdale, Fla. — (UPI) — A new all-purpose credit card is being launched by Credit Card Acceptance Corporation, according to J. C. Behringer, president. The Gold Medal credit cards will be honored initially by approximately 3,000 member establishments in more than 40 states.

Behringer believes that these feature will revolutionize the credit card industry.

...les company a means of crystal recovery.



New line of printing inks for use in paper trade will be manufactured in this plant at Greenville, S.C.

...letro-Atlantic ...xtile Products

...used for ...stripping. ...ro-Atlan... two sup... ...Ir. Buon... made in ...facturers ...package

...as devel... ...x type of ...chiefly in ...expected ...ig items. ...come one ...size to ...ns—used ...ness and

...unned ...n, Metro... ...plans to ...at Den...

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Operated for about 18 years is a Canadian facility, utilized chiefly for selling, but including some textile chemicals manufacture.

Metro-Atlantic additionally is working currently under license arrangements with manufacturing companies for the packaging and distribution of some of the products the firm produces in bulk. A household bleach, spot remover and spray glue are among these items.

The varied programs of the 25-year-old company are working together to bring expansion to the firm, Mr. Buonanno said. Employment has climbed to 130 throughout the organization with about 80 affiliated with the Centredale operation.

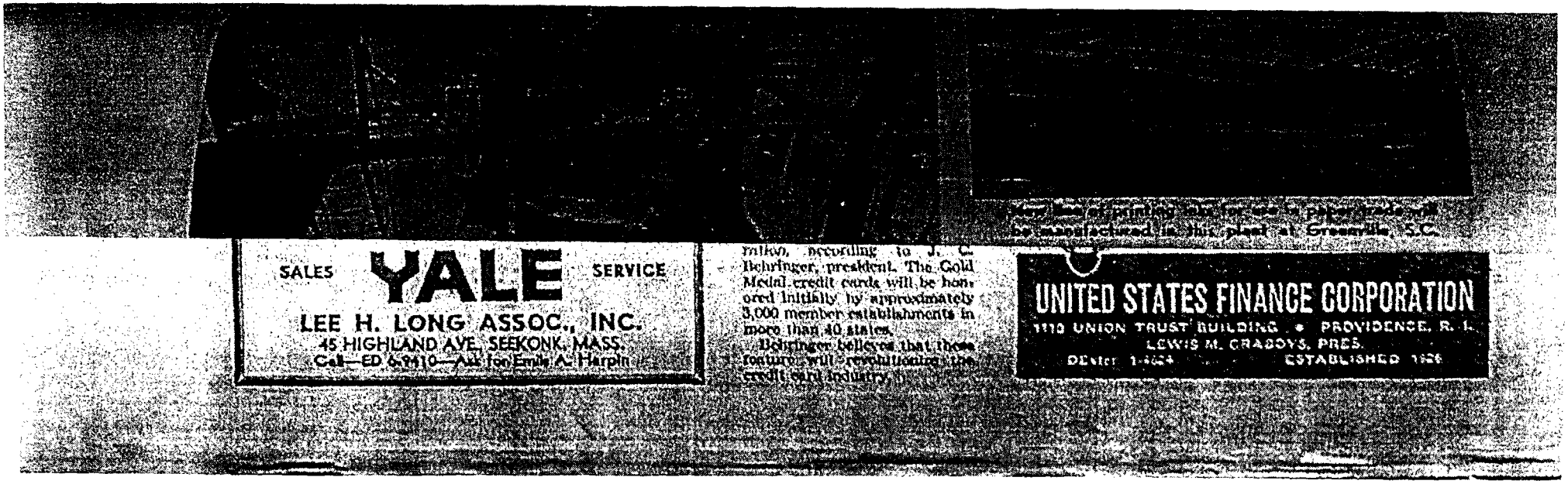
"We are looking forward to growth, especially from our entrance into the manufacture of products for the pharmaceutical trade, but we are striving also for a continuation of our employment stability record," Mr. Buonanno said. He reported that throughout its 25 years of operation the company has never laid off anyone.

Militar...

PLAINTIFF'S EXHIBIT

4

CLEARY - 2/10/03



talks), according to J. C. Behringer, president. The Gold Medal credit cards will be honored initially by approximately 3,000 member establishments in more than 40 states.

Behringer believes that these features will revolutionize the credit card industry.

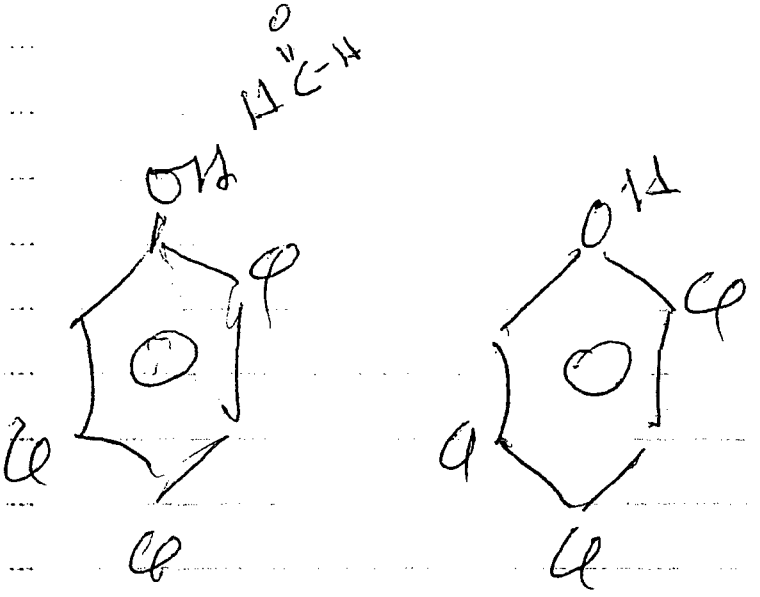
—Journal-Bulletin Photos by H. RAYMOND BALL

Upper level of new hexachlorophene plant at Metro-Atlantic, Inc., Centredale, showing a number of its stainless steel low and high temperature reactors.

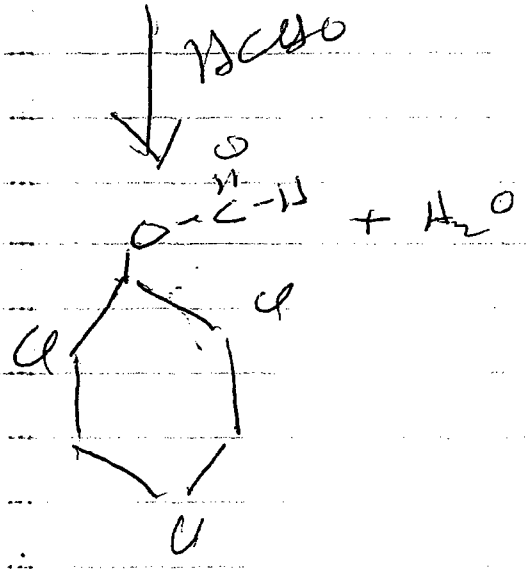
PLAINTIFF'S EXHIBIT 5

Large perforate centrifuge located in new plant provides company a means of crystal recovery.

PLAINTIFF'S
EXHIBIT
6
CLEAR4 - 2/10/03



TCP TCP



PLAINTIFF'S EXHIBIT 7
CLEARY - 2/10/03

6/8/64

ZEP Manufacture

Phase #1:

Purification Equipment:

Steel tank equipped with cooling jacket and gate type agitator and centrifuge.

Basic Charge:

Lbs.	Materials
--	Sodium TCP (Concentration 36-38%) So as to contain 1000 lbs. TCP contained
5280	30% Caustic Soda
600	30% Caustic Soda (Wash)
450	66° Be' Sulfuric Acid (Precipitating acid)
370	66° Be' Sulfuric Acid (Purification acid)
4800	Perchloroethylene
10	Nuchar
10	Fiber Flo
1000	Theo. Yield (Total Isomers)
787	Minimum Yield TCP
880	Maximum Yield TCP
65°C	Melting Point (Minimum)

PLAINTIFF'S EXHIBIT 3 CLEARY-Hoyle

This is Geo Hases
B.M of MATERIALS for
Purification of Trichlorophenol

"Zep" was our nickname
for Hexachlorophene.

To: Mr. Vincent Buonanno, c/o Temple Steel Co.; from Tom Cleary

CLARITY, INC. 45451 SOUTH CASPAR DRIVE / BOX 949 MENDOCINO, CALIFORNIA 95460 / TEL. 707 964-7065
FAX 707-937-2631

Vinny—

Among perhaps relevant matters not covered, 12/3:

Several years ago, the Newark, N.J. premises of Diamond-Alkali—long inactive and vacant, I believe, were declared to be a "superfund site", and were eventually cleaned up.

The person who knows the history and fate of D.-A. is John Burton, who resides in Washington, N.J. Tel. No. 905-689-6648. Burton was mgr. of that D.-A. plant when Mat.-Aff. was purchasing their TCP. He was seriously injured there ('60?) in a reactor explosion of a kind that also occurred also at Monsanto, Thompson, and the notorious Seveso, Italy event ('76-Givaudan/Roche)

I presume Burton also knows who paid for cleaning up that property, in Newark.

Question: If party A sells and ships Poison X to party B, who is unaware of it, who is responsible for the harm done by Poison X?

I look forward to receiving your "chemical list." I had been intending to request it, and I'll respond to it as soon as I'm able.

TOM

PLAINTIFF'S EXHIBIT 9
CLEARY - 2/10/03

To: Mr. Vincent Bacamonte % Temple Steel Co., From Tom Cleary

CLARITY, INC. 45451 SOUTH CASPAR DRIVE / BOX 949 MENDOCINO, CALIFORNIA 95460 / TEL. 707 964-7065

Dear Vince,

You're aware I'm sure of my conversation some time ago with Deming S. concerning the soil analyses At Centredale. It might be well to depart my chemist-to-lawyer impressions with chemist-to-operating-man reports:

1. I was startled by the number of substances that showed up in these samples.
2. The only ones I have knowledge of are Dioxin and Perchloroethylene.
3. The only Metro operation I was familiar with was "Reserve Silt", which I sold for them. This consumed large amounts of Nitrobenzene, NOT found.
4. No trace of the Lilly work, ie. "Tretlan" or its Dinitro intermediate or it's raw materials were found.

Except for "Reserve Silt" and the two projects I was involved with, I knew nothing about the operations, products, raw materials used at Metro.

I have no knowledge of the origin of PCB's, etc. etc. found in these samples.

Best regards,

Tom

PLAINTIFF'S EXHIBIT 10
CLEARY - 2/10/03

State of California)
County of Mendocino) ss:

AFFIDAVIT OF THOMAS F. CLEARY

Thomas F. Cleary, being duly sworn, deposes and states as follows:

1. I have personal knowledge of the facts set forth in this affidavit and, if called as a witness, I could and would competently testify to the facts set forth below.

2. I am retired after a career working for several companies as an organic chemist.

3. I currently reside at 45451 S. Caspar Dr., Mendocino, CA 95460, phone 707-964-7065.

4. I have a B.S. in chemistry from Rutgers University.

5. Before my retirement, I was employed at Centerchem, Inc. between approximately 1960 to 1980 as an organic chemist and as President and Chief Executive Officer after 1977.

6. While working for Centerchem, Inc., I would solicit custom chemical manufacturing contracts for small chemical manufacturing companies.

7. As part of that work, I would assist the chemical manufacturers with development of the manufacturing processes used to fill their custom chemical manufacturing contracts.

8. In the 1960s I was acquainted with Metro-Atlantic, Inc., a chemical manufacturer located in North Providence, Rhode Island.

9. Metro-Atlantic was owned and run by Joseph Buonanno, now deceased.

10. I was acquainted with purchasing agents of Eli Lilly and Company of Indianapolis, IN and would attempt to assist in the development of contracts for the custom manufacture of chemicals for Eli Lilly by custom chemical manufacturing companies like Metro-Atlantic.

11. My primary contacts at Eli Lilly in the 1960s were Robert G. "Bob" Weigel, Eli Lilly's purchasing agent, now deceased, and assistant purchasing agent Robert Dille, also deceased.

12. In approximately 1963 or 1964, I became aware of Eli Lilly's development of a pesticide known as treflan or trifluralin.

13. When starting production of treflan, Eli Lilly needed time to design, build and start up the process equipment in its Tippecanoe, IN plant.

14. I suggested to Joseph Buonanno that Metro-Atlantic might be able to manufacture treflan for Eli Lilly.

15. I assisted Metro-Atlantic in developing the process to manufacture treflan at its North Providence, Rhode Island plant and Metro-Atlantic erected a building specifically to house that process at that time.

16. Eli Lilly entered into an agreement with Metro-Atlantic by which Metro-Atlantic made treflan for Eli Lilly at the Metro-Atlantic North Providence plant.

17. The treflan process at the North Providence plant consisted of converting the substrate parachlorobenzotrifluoride or PCBT, obtained from Hooker Chemical in Niagara Falls, N.Y., into treflan, first by dinitration then amination of the resulting 3.5-Dinitro-4-chlorobenzotifluoride with dipropylamime. The treflan active substance was formulated with solvents and emulsifiers supplied by and under the direction of Eli Lilly.

18. After a short period of production, no more than a few months at most, Eli Lilly began production of treflan at its Tippecanoe, IN plant and treflan production at the Metro-Atlantic North Providence, R.I. plant ceased.

19. The Metro-Atlantic production facility built for treflan production was not used for

some time after the treflan production ceased; I then worked with Joseph Buonanno to set up a process to manufacture hexachlorophene in the building formerly used to manufacture treflan.

20. The hexachlorophene produced by Metro-Atlantic was sold on the open market, with Sterling Winthrop being one of the largest purchasers.

21. To my knowledge, Eli Lilly had no relationship to the production of hexachlorophene at the Metro-Atlantic North Providence plant.

Further affiant sayeth not.

[name]

Subscribed to and sworn to before me this
8 day of ~~September~~ November, 2001.

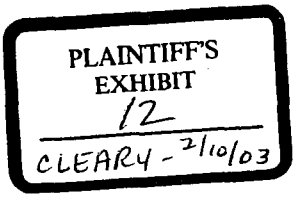
My commission expires: 10-5-03

JACK R. DRUCKER
COMM. 1238809 MEN. RC81
NOTARY PUBLIC
CALIFORNIA
MENDOCINO COUNTY
MY COMM. EXPIRES OCT. 5, 2003

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION I
ONE CONGRESS STREET SUITE 1100
BOSTON, MASSACHUSETTS 02114-2023

Memorandum

DRAFT



Date: November 26, 2002

Subj: Notes of Conversation with Thomas Cleary

From: Ann Gardner
Paralegal

To: Centredale Manor Site File

On Thursday November 14, 2002 I placed a call to Thomas Cleary of Mendocino, CA to inquire if he recalled how Metro-Atlantic produced hexachlorophene. These notes have been reviewed by Mr. Cleary for accuracy and is a summary of our conversation.

Background

Mr. Cleary was an organic and production chemist which means that he supplied chemical companies with the production "know-how" for specific chemicals. He would work closely with the companies during the process development stage.

He was aware that the Eli Lilly company had developed a chemical called Treflan and was looking for a place to manufacture this substance until a permanent facility was constructed. Mr. Cleary was aware of the Metro-Atlantic facility and brokered a deal for Metro-Atlantic to produce Treflan for Eli Lilly. According to Mr. Cleary, Metro-Atlantic

constructed a separate building for the production of Treflan. When asked why Metro-Atlantic went to the effort and expense of constructing a building for a temporary production process, Mr. Cleary thought that the building was not a big investment and that it was profitable for Metro-Atlantic. Mr. Cleary estimated that the production of Treflan at the Metro-Atlantic facility was less than a year.

Hexachlorophene production

After the Treflan production ceased, Mr. Cleary worked with Metro-Atlantic to produce hexachlorophene. At the time, there was only one company that produced hexachlorophene and companies were looking for additional suppliers.

Hexachlorophene is manufactured using 2,4,5-trichlorophenol. At the time Metro-Atlantic began hexachlorophene production, the U.S. Army was using large quantities of trichlorophenol in the production of Agent Orange making quantities of ~~pure~~ 2,4,5-trichlorophenol unavailable. Metro-Atlantic purchased a crude form of 2,4,5-trichlorophenol from Diamond Alkali. This was a dark liquid brought into the facility by tanker trucks. Before the 2,4,5-trichlorophenol could be used in hexachlorophene production, it needed to be purified. This was accomplished by adding sodium hydroxide and methyl alcohol to 2,4,5-trichlorophenol. There was not 100% recovery from the purification process and some 2,4,5-trichlorophenol became a waste or by-product. Mr. Cleary believes that this waste 2,4,5-trichlorophenol is the origin of the dioxin at the

Centredale Superfund Site. However, Mr. Cleary is very puzzled as to why phenols are not present in the sampling results.

Mr. Cleary explained how Diamond Alkali produced the 2,4,5-trichlorophenol. The raw material, 1,2,4,5-tetrachlorobeneze was put into an autoclave, a ~~machine~~ vessel that puts substances under very high temperatures and pressure, and converts the 1,2,4,5-tetrachlorobenzene into 2,4,5-trichlorophenol. Mr. Cleary suggested we contact John Burton, formerly with Diamond Alkali, to ask questions about this process and the 2,4,5-trichlorophenol delivered to Metro-Atlantic.

Tel: 908-659-6648

Once the 2,4,5-trichlorophenol was purified, it was ~~mixed~~ reacted with formaldehyde to create hexachlorophene. Mr. Cleary has a patent on this production of hexachlorophene. Mr. Cleary was certain that the hexachlorophene production resulted in the dioxin at the site. As previously mentioned, the 2,4,5-trichlorophenol purification process did not recapture all of the 2,4,5-trichlorophenol and some was lost as a waste by-product. This waste would contain, among other things, dioxin and phenols. He repeatedly stated he was puzzled as to why no phenols were appearing in the test results.

I asked Mr. Cleary about the Metro-Atlantic plant and who might have knowledge of the hexachlorophene process. Apparently, hexachlorophene was really the only chemical they produced; the other chemical work done by Metro-Atlantic was primarily mixing and

re-formulating products. Other than Mr. Cleary, all the individuals who were familiar with the hexachlorophene production are deceased. Joseph ("Joe") Buonanno, Sr. was the head of Metro-Atlantic and became a good friend of Mr. Cleary's. George ~~Ewes (sp?)~~ HUSE was active in managing the hexachlorophene production and moved to South Caroiina * when Metro-Atlantic opened the plant there. Unfortunately both are deceased. Joseph Buonanno, Jr. was in the sales department and did not or would not have any detailed knowledge of the production process. Mr. Cleary recalled Joe Buonanno had two partners: Hugh Bonino and Bernard ("Bernie") Buonanno. Bernie would be at the plant but Mr. Cleary did not recall what he did. Mr. Bonino moved to South Carolina when Metro-Atlantic opened a plant there but has since passed away.

* Prior to the move to Greenville, S.C. Metro-Atlantic merged with Crown Chemical Co, A similar business in R.I. The merged entity, Known As "Crown-Metro" was purchased by United Shoe Machinery Corp and then by a succession of other owners, including, finally, Black & Decker.
TC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 1
1 CONGRESS STREET, SUITE 1100
BOSTON, MASSACHUSETTS 02114-2023

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

November 26, 2002

Thomas Cleary
45451 S. Caspar Drive
Mendocino, CA 95460

Dear Mr. Cleary,

Enclosed is a draft summary of my conversation with you concerning the Metro-Atlantic facility, formerly located in North Providence, RI. Our discussion centered around their use of 2,4,5-trichlorophenol in the production of hexachlorophene. Because of the chemistry involved, you agreed to review my notes to ensure that I had the facts correct. Please make corrections wherever necessary. If there is any information you would like to add, please do so. I have enclosed a self-addressed, stamped envelope so you may return the letter to us

Thank you very much for you time. If you would like to discuss this memo or any other issue concerning the Metro-Atlantic facility, New England Container Company, or the Centredale Manor Restoration Project, please contact me at (617) 918-1895 and I will return your call, or you can reach me via e-mail at gardner.ann@epa.gov.

Sincerely,

Ann Gardner

617-918-1895

Ann L. Gardner,
Paralegal

Enclosure

PLAINTIFF'S EXHIBIT
13
CLEARY - 2/10/03

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 1
1 CONGRESS STREET, SUITE 1100
BOSTON, MASSACHUSETTS 02114-2023

CERTIFIED MAIL -
RETURN RECEIPT REQUESTED

January 14, 2003

Thomas Cleary
45451 South Caspar Dr.
Mendocino, CA 95460

Re: Notes concerning use of 2,4,5-trichlorophenol at Centredale Manor Site File, North Providence, RI

Dear Mr. Cleary,

Enclosed you will find a copy of my draft memo to the file concerning our phone conversation in November 2002. In addition, I have also enclosed a photocopy of the notes and corrections you sent back to me.

When I revise my draft memo, I will send you that version for your review and comment.

Thank you for your time and assistance in this matter. If you have any questions, do not hesitate to call me at (617) 918-1895.

Sincerely,

Ann L. Gardner

Ann L. Gardner
Paralegal

Enclosure

PLAINTIFF'S EXHIBIT
14
CLEARY - 2/10/03

12/02/02

Dear Ms. Gardner

Herewith a number of corrections to your notes, and some additional pertinent material.

(1) This is misleading. The dioxin, unknown and unsuspected, was already present in the crude TCP product shipped from Diamond Alkali Co. It was not chemically or physically possible that additional Dioxin could have been generated at the Centredale site.

(A) Co-option of the TCP supply began several months AFTER Hex production began at Centredale. What the USG bought was not TCP, but its downstream derivative, Trichlorophenyl-acetic Acid, all of which was made directly from CRude, unpurified TCP.

The amount of TCP supplied to M-A by Diamond Alkali, probably didn't exceed 25,000 Kgs.

PLAINTIFF'S EXHIBIT 15 CLEARY -2/10/03

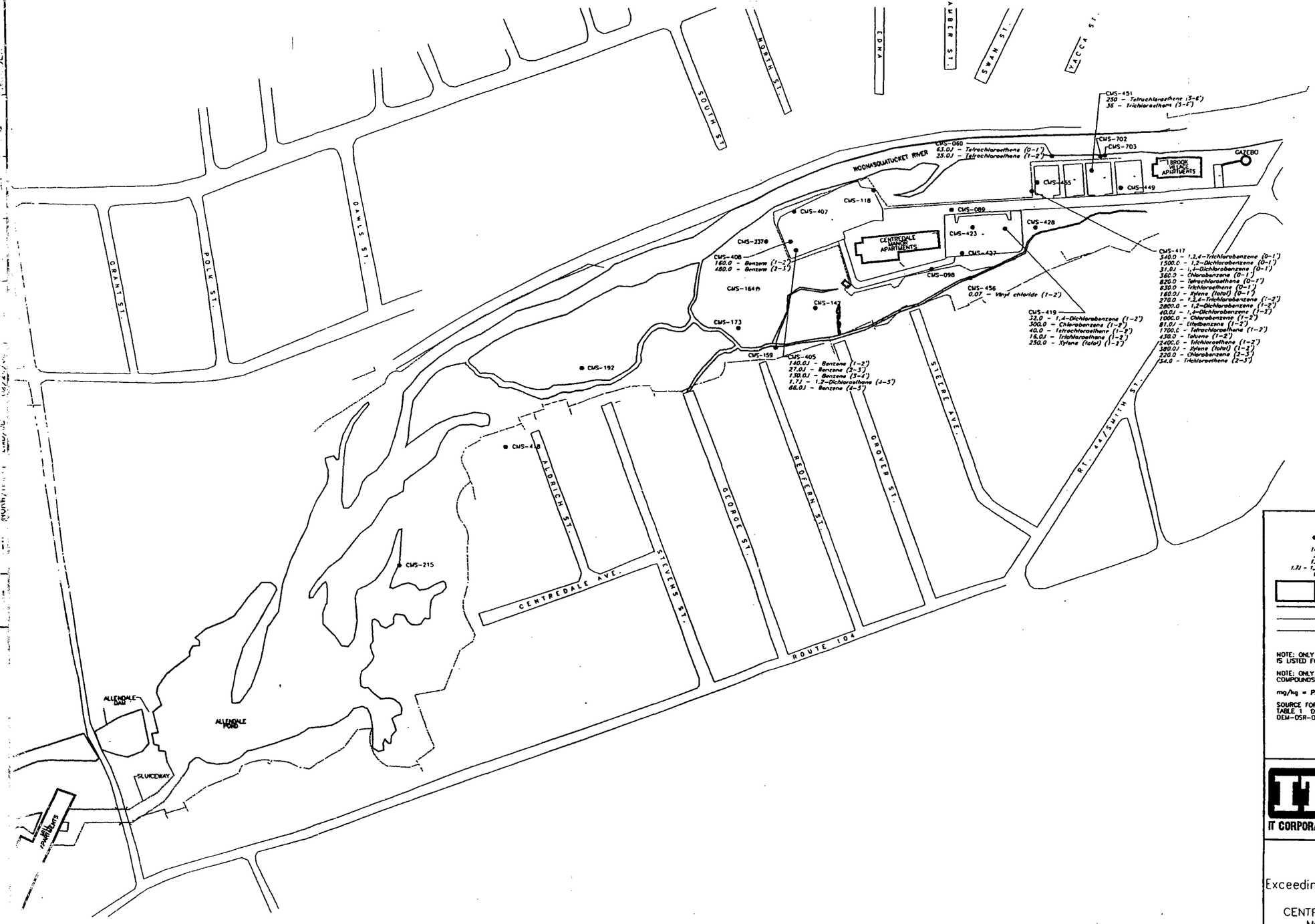
(2) Metro-Atlantic had in fact for some years, produced meta-Nitro-benzene Sodium Sulfonate by the Sulfonation of Nitrobenzene I had been selling this product for another company. It was the cessation of that source that led to my acquaintance with Mr. Buonanno and Metro-Atlantic in about '61.

The soil analyses at Centredal show no trace of this operation

Also, there was no trace found there of raw materials, intermediates or product, Related to the Triethy operation for Lilly.

Volatile Organic Compounds
Exceeding Rhode Island Residential Standards
(June to November 1999)

PLAINTIFF'S EXHIBIT 17 CLEARY - 2/10/03



LEGEND:

- SOIL BORING LOCATION
  - EX.: CMS-118 - SOIL BORING IDENTIFICATION
  - 140.0J - Benzene (1-2') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  - 27.0J - Benzene (2-3') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  - 130.0J - Benzene (3-4') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  - 1.7J - 1,2-Dichloroethane (4-5') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  - 66.0J - Benzene (4-5') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
- BUILDING OUTLINE
- WATERWAY OR POND
- ROADWAY EDGE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION FOR EACH COMPOUND EXCEEDANCE IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR VOLATILE ORGANIC COMPOUNDS ARE SHOWN.

mg/kg = PARTS PER MILLION

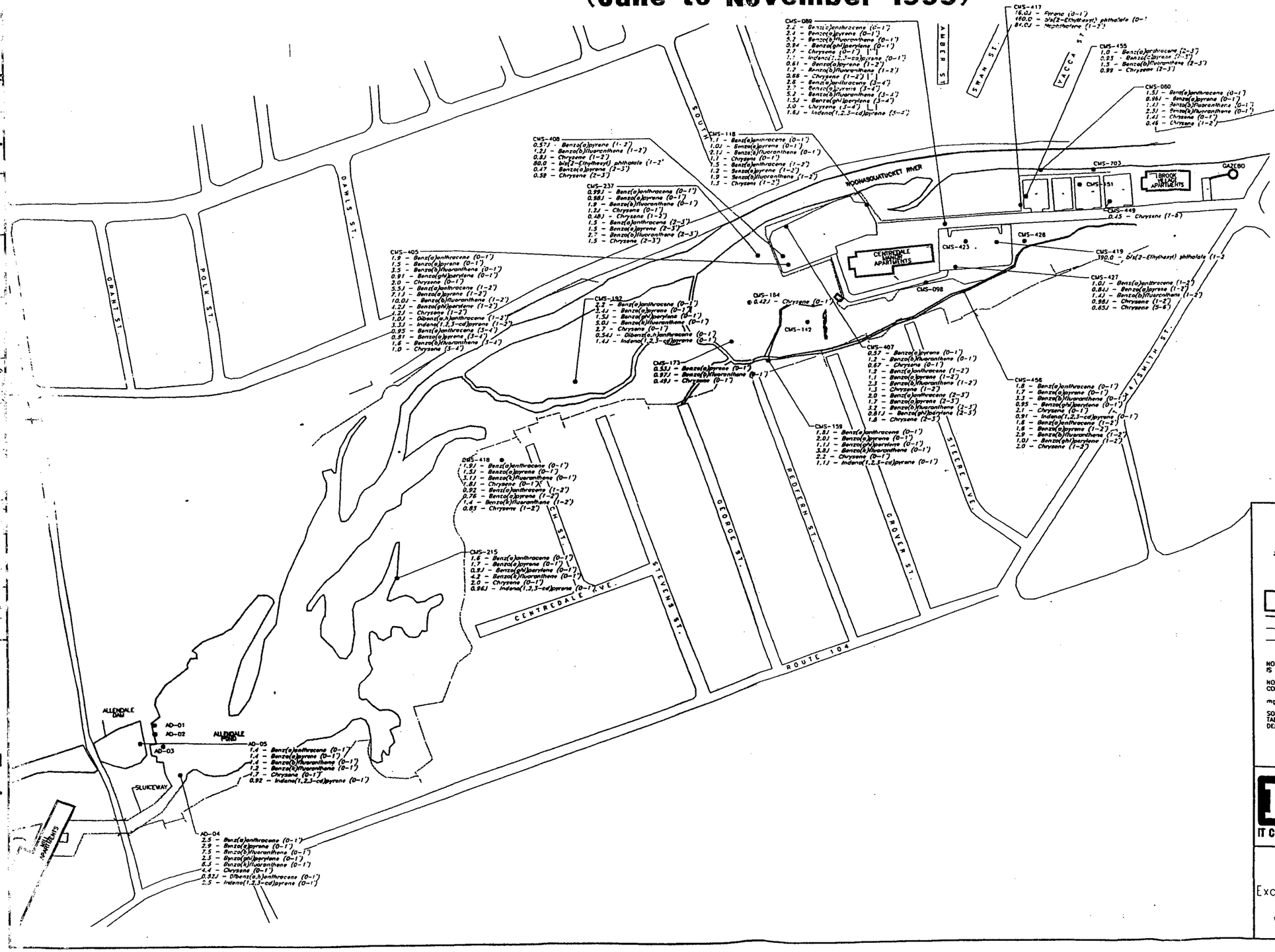
SOURCE FOR RHODE ISLAND STANDARDS:
TABLE 1 DIRECT EXPOSURE CRITERIA, REMEDIATION REGULATIONS.
DEM-OSR-01-93, 31 MARCH 1993, AMENDED AUGUST 1996

SCALE
0 125 250 375 FEET

IT CORPORATION
88C ELM STREET
HOPKINTON, MASSACHUSETTS
(508) 435-9561

FIGURE 2
Volatile Organic Compounds
Exceeding Rhode Island Residential Standards
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

Semi Volatile Organic Compounds
Exceeding Rhode Island Residential Standards
(June to November 1999)



LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-118 – SOIL BORING IDENTIFICATION
  1.1 – Benz(a)anthracene (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.0J – Benzo(a)pyrene (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  2.1J – Benzo(b)fluoranthene (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.1 – Chrysene (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.5 – Benz(a)anthracene (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.2 – Benzo(a)pyrene (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.9 – Benzo(b)fluoranthene (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  1.3 – Chrysene (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
- BUILDING OUTLINE
- WATERWAY OR POND
- ROADWAY EDGE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION FOR EACH COMPOUND EXCEEDANCE IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR SEMI VOLATILE ORGANIC COMPOUNDS ARE SHOWN.

mg/kg = PARTS PER MILLION

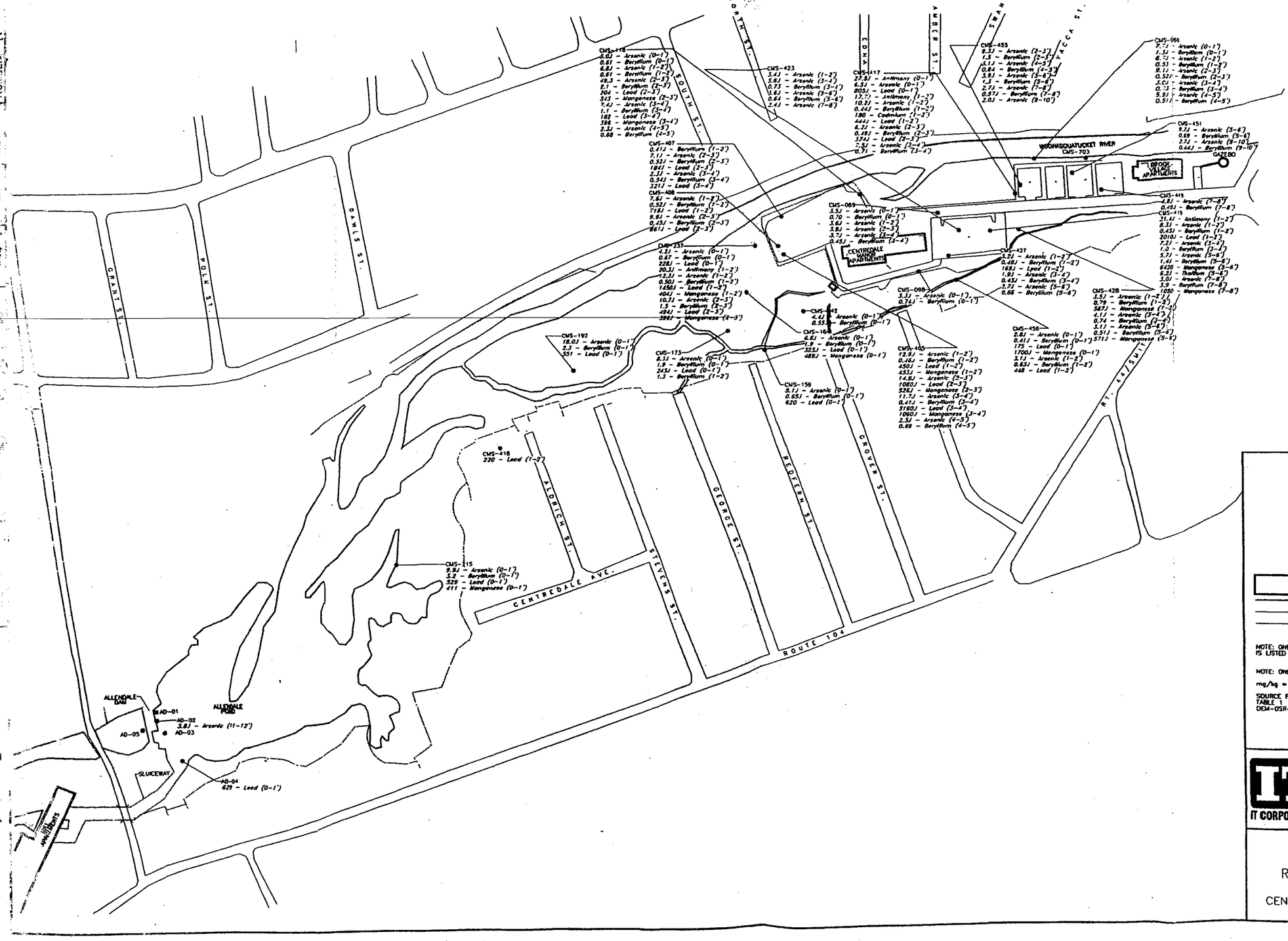
SOURCE FOR RHODE ISLAND STANDARDS:
TABLE 1 DIRECT EXPOSURE CRITERIA, REMEDIATION REGULATIONS.
DEM-DSR-01-93, 31 MARCH 1993, AMENDED AUGUST 1996

SCALE
0 125 250 375 FEET

IT CORPORATION
88C ELM STREET
HOPKINTON, MASSACHUSETTS
(508) 435-9561

FIGURE 3
Semi Volatile Organic Compounds
Exceeding Rhode Island Residential Standards
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

RCRA Metals Exceeding Rhode Island Residential Standards (June to November 1999)



LEGEND:

- SOIL BORING LOCATION
  - EX.: CMS-118 – SOIL BORING IDENTIFICATION
  - 5.6J – Arsenic (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 0.61 – Beryllium (0-1') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 6.8J – Arsenic (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 0.81 – Beryllium (1-2') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 48.3 – Arsenic (2-3') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 2.1 – Beryllium (2-3') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 204 – Lead (2-3') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 543 – Manganese (2-3') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 7.4J – Arsenic (3-4') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 1.7 – Beryllium (3-4') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 182 – Lead (3-4') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 596 – Manganese (3-4') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 2.3J – Arsenic (4-5') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
  - 0.88 – Beryllium (4-5') – SAMPLE RESULT AND COMPOUND IN mg/kg – SAMPLE DEPTH RANGE
- BUILDING OUTLINE
- WATERWAY OR POND
- ROADWAY EDGE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION FOR EACH COMPOUND EXCEEDANCE IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR RCRA METALS ARE SHOWN.

mg/kg = PARTS PER MILLION

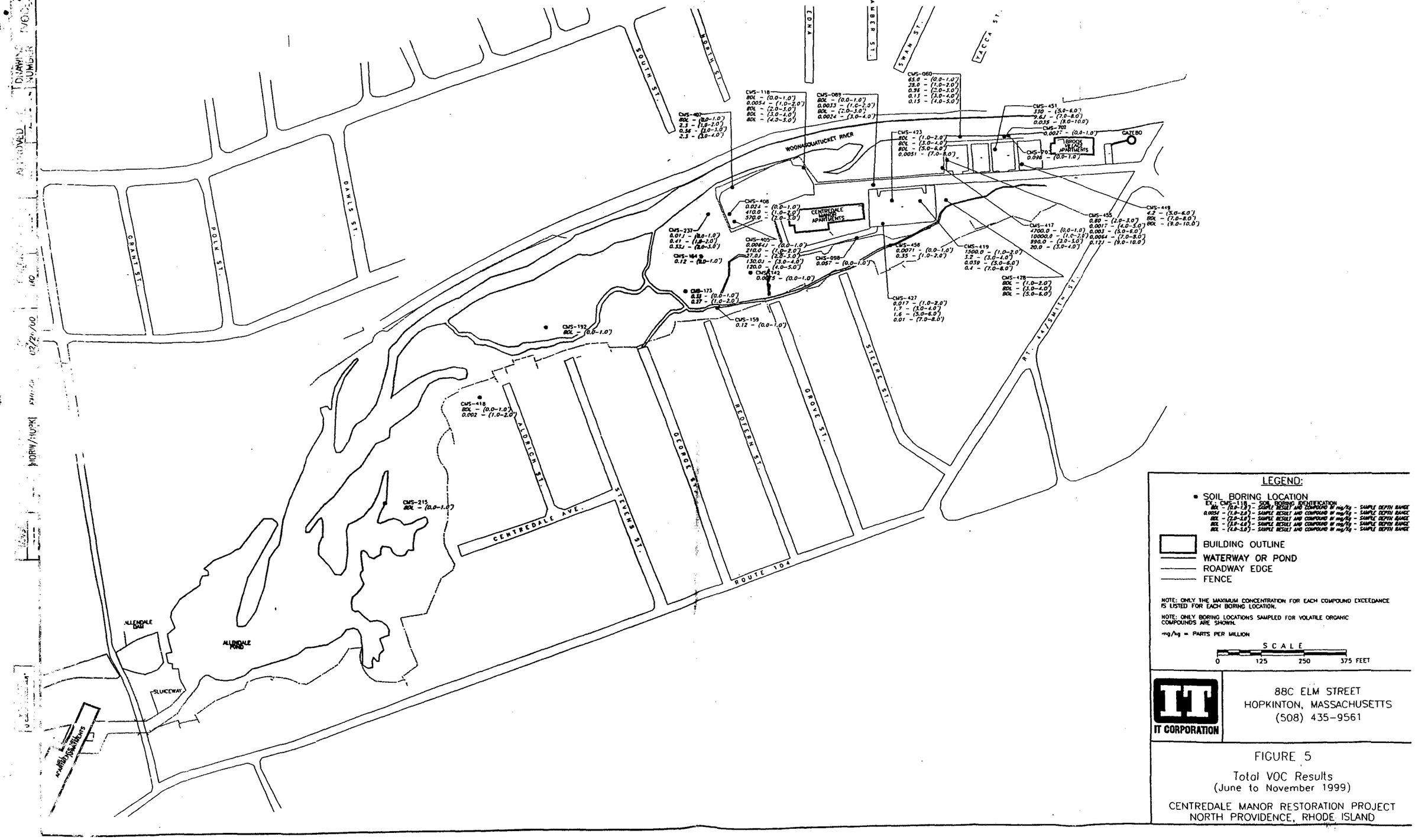
SOURCE FOR RHODE ISLAND STANDARDS:
TABLE 1 DIRECT EXPOSURE CRITERIA, REMEDIATION REGULATIONS, DEM-DSR-01-93, 31 MARCH 1993, AMENDED AUGUST 1996

SCALE
0 125 250 375 FEET

IT CORPORATION
88C ELM STREET
HOPKINTON, MASSACHUSETTS
(508) 435-9561

FIGURE 4
RCRA Metals Exceeding
Rhode Island Residential Standards
(June to November 1999)
CENTREDALE MANOR RESTORATION; PROJECT
NORTH PROVIDENCE, RHODE ISLAND

Total VOC Results
(June to November 1999)



LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-118 - SOIL BORING IDENTIFICATION
  BDL - (0.0-1.0') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  0.0054 - (1.0-2.0') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  BDL - (2.0-3.0') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  BDL - (3.0-4.0') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
  BDL - (4.0-5.0') - SAMPLE RESULT AND COMPOUND IN mg/kg - SAMPLE DEPTH RANGE
- BUILDING OUTLINE
- WATERWAY OR POND
- ROADWAY EDGE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION FOR EACH COMPOUND EXCEEDANCE IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR VOLATILE ORGANIC COMPOUNDS ARE SHOWN.

mg/kg = PARTS PER MILLION

SCALE
0 125 250 375 FEET

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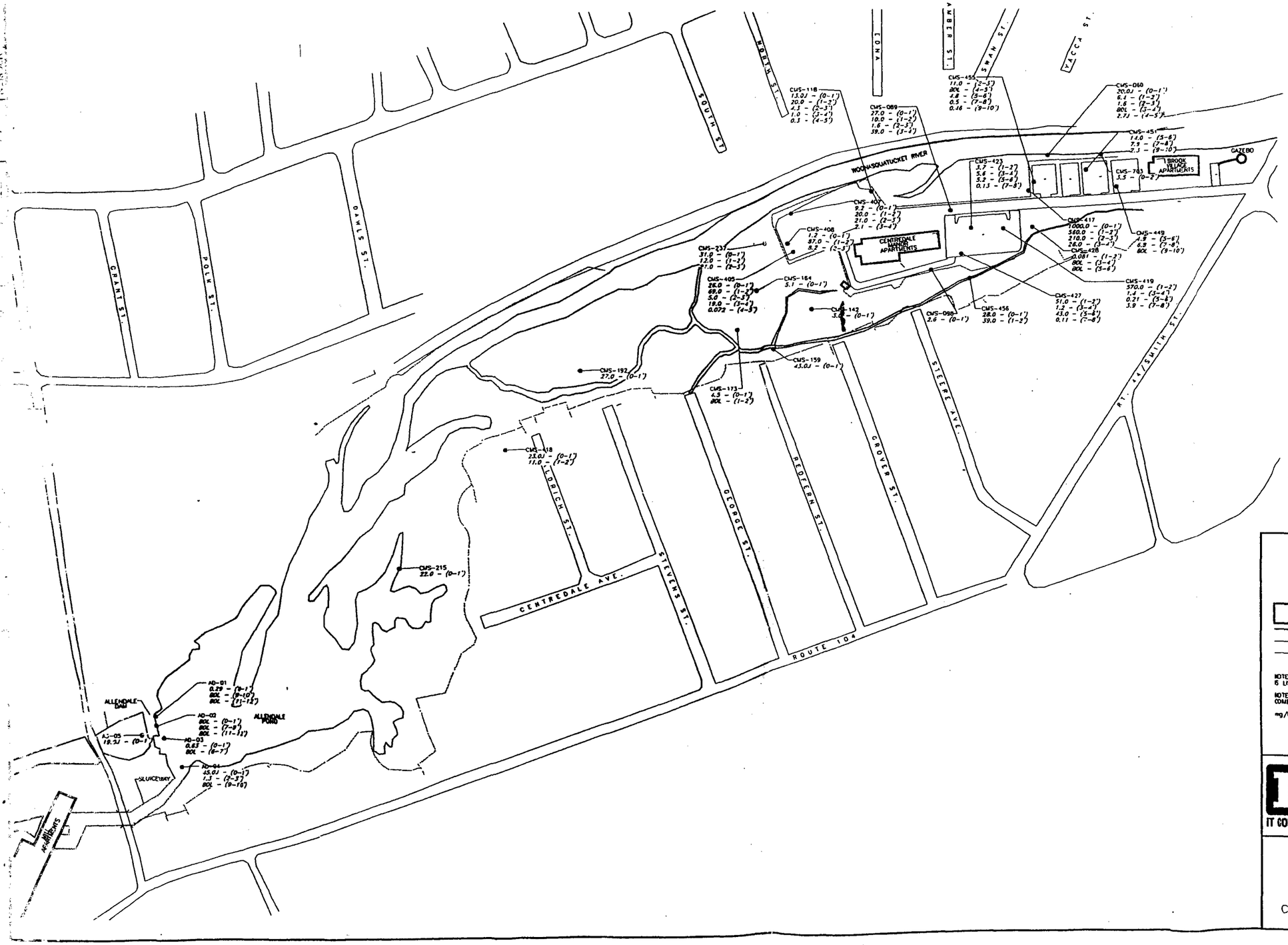
FIGURE 5

Total VOC Results
(June to November 1999)

CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

Total SVOC Results
(June to November 1999)



LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-118 - SOIL BORING IDENTIFICATION
  13.0J - (0-1') - SAMPLE RESULT AND COMPOUND BY mg/kg - SAMPLE DEPTH RANGE
  20.0 - (1-2') - SAMPLE RESULT AND COMPOUND BY mg/kg - SAMPLE DEPTH RANGE
  4.3 - (2-3') - SAMPLE RESULT AND COMPOUND BY mg/kg - SAMPLE DEPTH RANGE
  1.0 - (3-4') - SAMPLE RESULT AND COMPOUND BY mg/kg - SAMPLE DEPTH RANGE
  0.3 - (4-5') - SAMPLE RESULT AND COMPOUND BY mg/kg - SAMPLE DEPTH RANGE

BUILDING OUTLINE
WATERWAY OR POND
ROADWAY EDGE
FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION FOR EACH COMPOUND EXCEEDANCE IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR SEMI VOLATILE ORGANIC COMPOUNDS ARE SHOWN.

mg/kg = PARTS PER MILLION

SCALE
0 125 250 375 FEET

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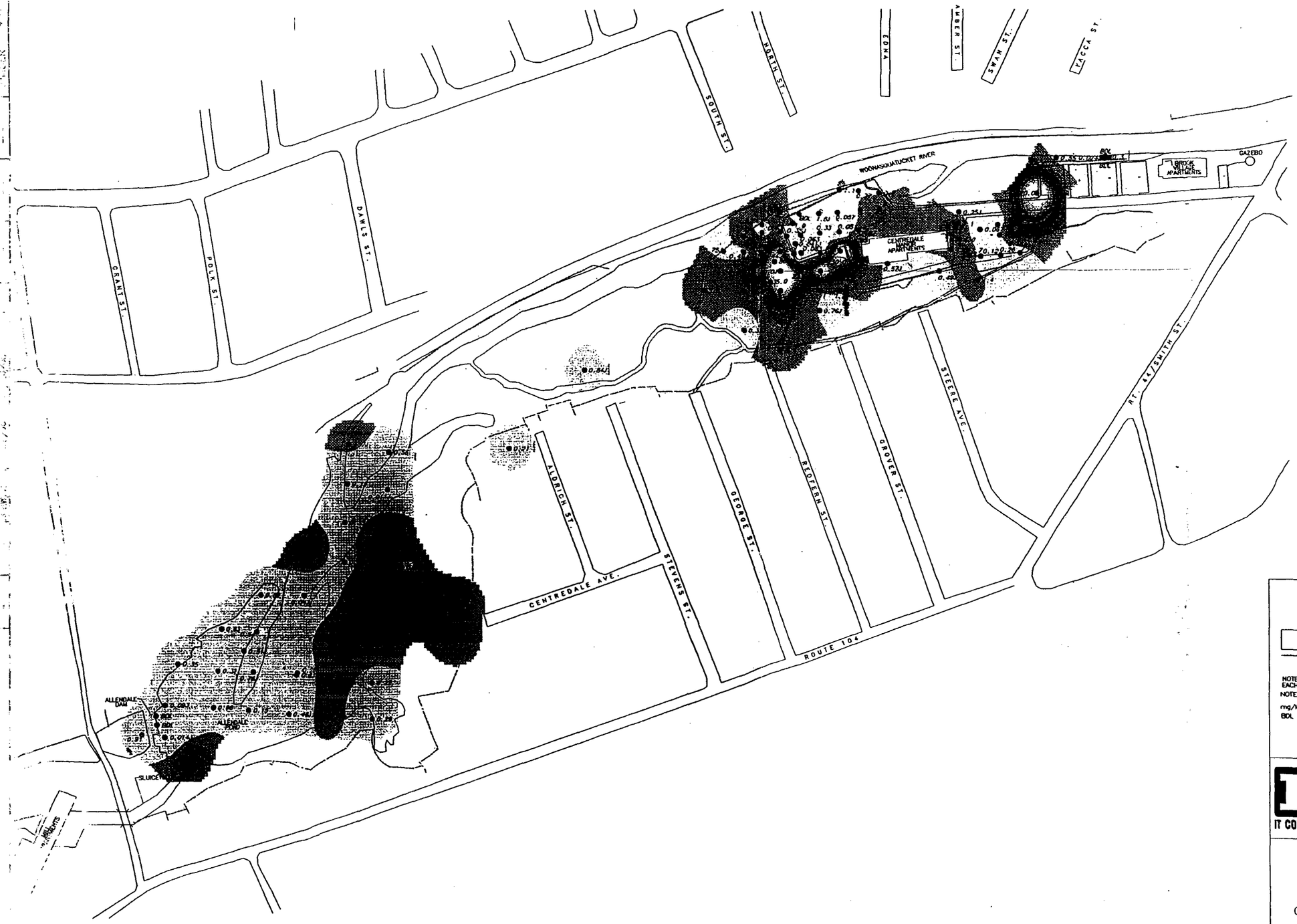
FIGURE 6

Total SVOC Results
(June to November 1999)

CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PCB Concentration Distribution in Soil
(0-1 feet below ground surface)
(June to November 1999)



5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0

Concentrations in milligrams per kilogram (mg/Kg)

LEGEND:

- SOIL BORING LOCATION
  4.1 - SAMPLE RESULT IN mg/Kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.
NOTE: ONLY BORING LOCATIONS SAMPLED FOR PCBS ARE SHOWN.
mg/kg = PARTS PER MILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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FIGURE 7a
PCB Concentration Distribution in Soil
(0-1 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PCB Concentration Distribution in Soil
(1-2 feet below ground surface)
(June to November 1999)

5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0

Concentrations in milligrams per kilogram (mg/Kg)

LEGEND:

- SOIL BORING LOCATION
  32.0- SAMPLE RESULT IN mg/Kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.
NOTE: ONLY BORING LOCATIONS SAMPLED FOR PCBS ARE SHOWN.
mg/kg = PARTS PER MILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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FIGURE 7b
PCB Concentration Distribution in Soil
(1-2 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PCB Concentration Distribution in Soil
(2-3 feet below ground surface)
(June to November 1999)

5000
4000
3000
2000
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0

Concentrations in
milligrams per kilogram (mg/Kg)

LEGEND:

- SOIL BORING LOCATION
  0.33J - SAMPLE RESULT IN mg/kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.
NOTE: ONLY BORING LOCATIONS SAMPLED FOR PCBS ARE SHOWN.

mg/kg = PARTS PER MILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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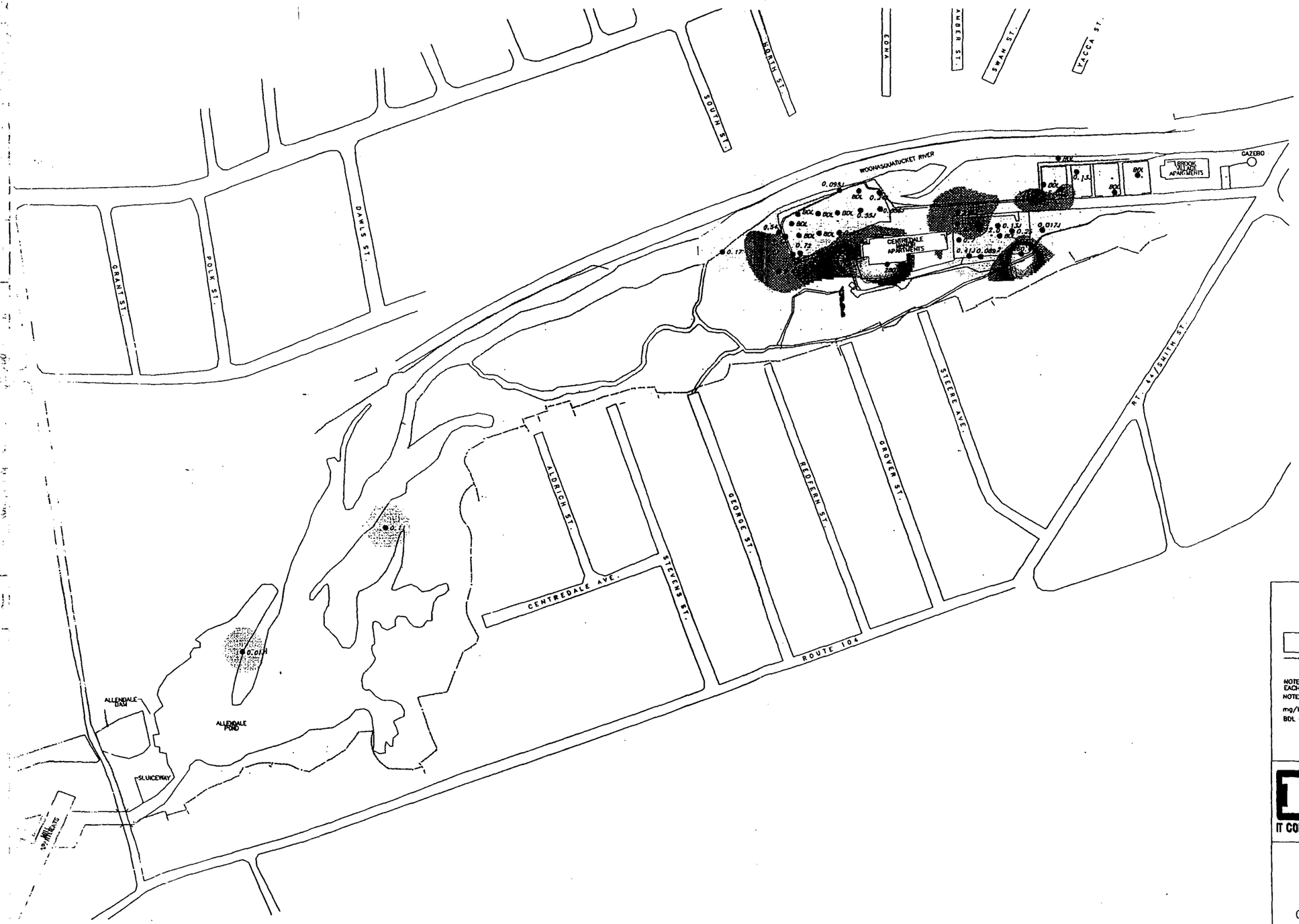
FIGURE 7c
PCB Concentration Distribution in Soil
(2-3 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PCB Concentration Distribution in Soil
(3-4 feet below ground surface)
(June to November 1999)



5000 4000 3000 2000 1000 900 800 700 600 500 400 300 200 100 90 80 70 60 50 40 30 20 10 9 8 7 6 5 4 3 2 1 0

Concentrations in
milligrams per kilogram (mg/Kg)

LEGEND:

- ●SOIL BORING LOCATION
  2.4- SAMPLE RESULT in mg/Kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.
NOTE: ONLY BORING LOCATIONS SAMPLED FOR PCBS ARE SHOWN.
mg/kg = PARTS PER MILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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FIGURE 7d
PCB Concentration Distribution in Soil
(3-4 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PCB Concentration Distribution in Soil
(4-8 feet below ground surface)
(June to November 1999)

LEGEND:

- ● SOIL BORING LOCATION
  EX.: CMS-155 - SOIL BORING IDENTIFICATION
- 1 ppm
- 10 ppm
- RED 4-5 FEET
- GREEN 5-6 FEET
- BLUE 6-7 FEET
- CYAN 7-8 FEET
- BUILDING OUTLINE
- FENCE

SCALE
0 125 250 375 FEET

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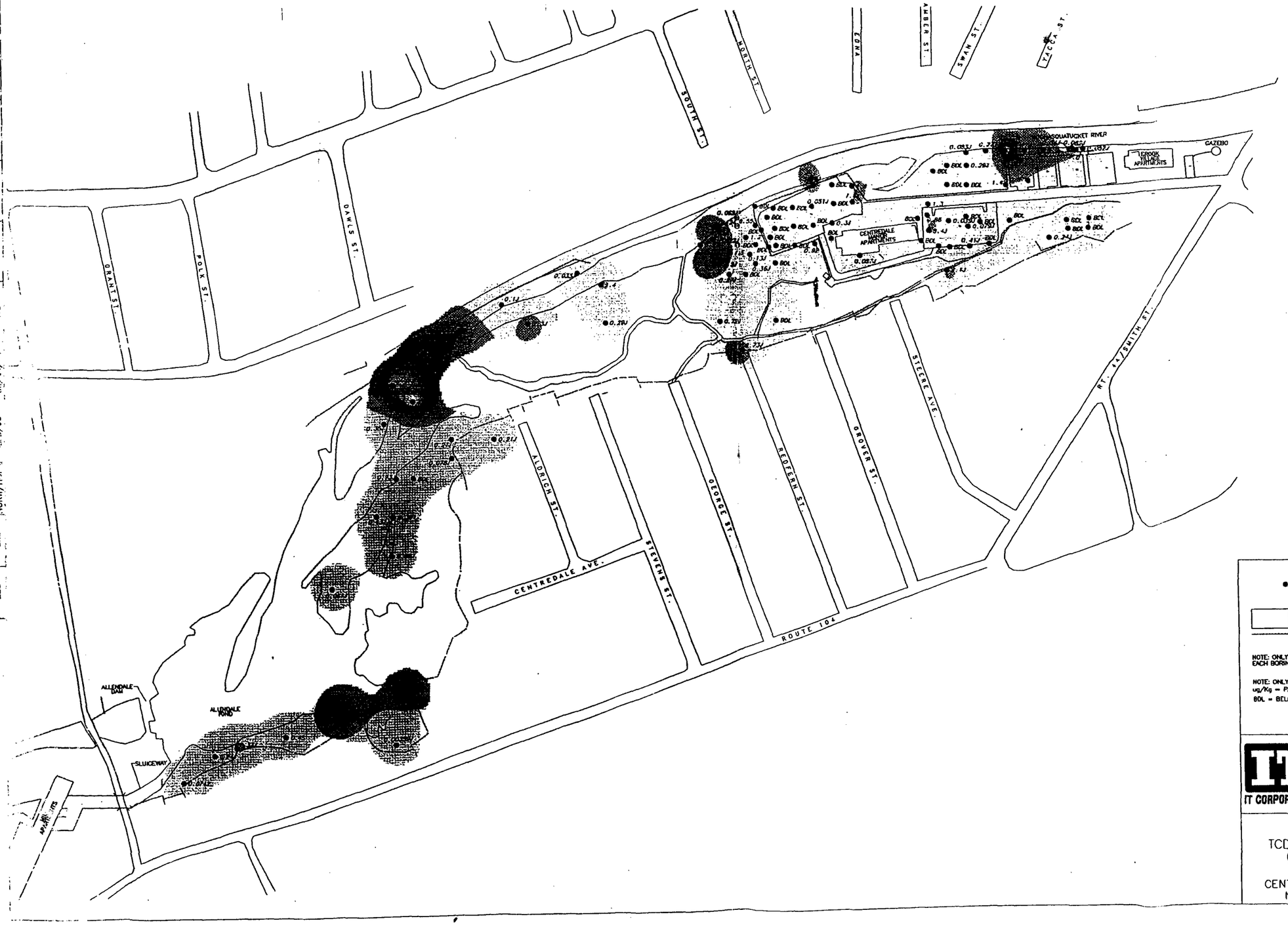
FIGURE 7e
PCB Concentration Distribution in Soil
(4-8 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

TCDD Concentration Distribution in Soil
(1-2 feet below ground surface)
(June to November 1999)

PLAINTIFF'S EXHIBIT
16
CLEARY - 2/10/03



Site Action Level

500 400 300 200 100 90 80 70 60 50 40 30 20 10 9 8 7 6 5 4 3 2 1 0

Concentrations in micrograms per kilogram (ug/Kg)

LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-118 - SOIL BORING IDENTIFICATION
  0.24J - SAMPLE RESULT IN ug/Kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR DIOXIN ARE SHOWN.
ug/Kg = PARTS PER BILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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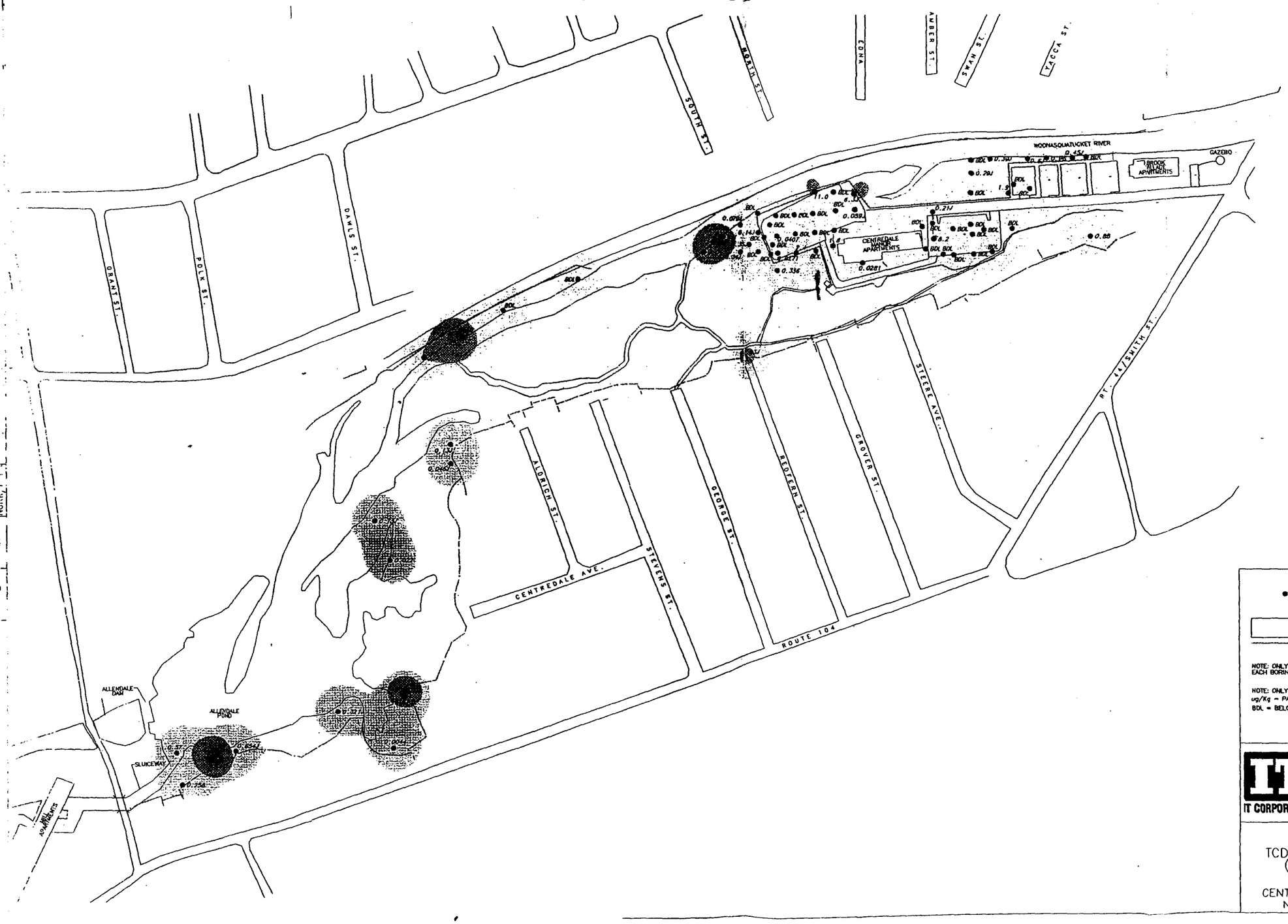
FIGURE 8b
TCDD Concentration Distribution in Soil
(1-2 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

TCDD Concentration Distribution in Soil
(2-3 feet below ground surface)
(June to November 1999)



Site Action Level

500 400 300 200 100 90 80 70 60 50 40 30 20 10 9 8 7 6 5 4 3 2 1 0

Concentrations in micrograms per kilogram (ug/Kg)

LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-118 - SOIL BORING IDENTIFICATION
  0.88 - SAMPLE RESULT in ug/kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR DIOXIN ARE SHOWN.
ug/Kg = PARTS PER BILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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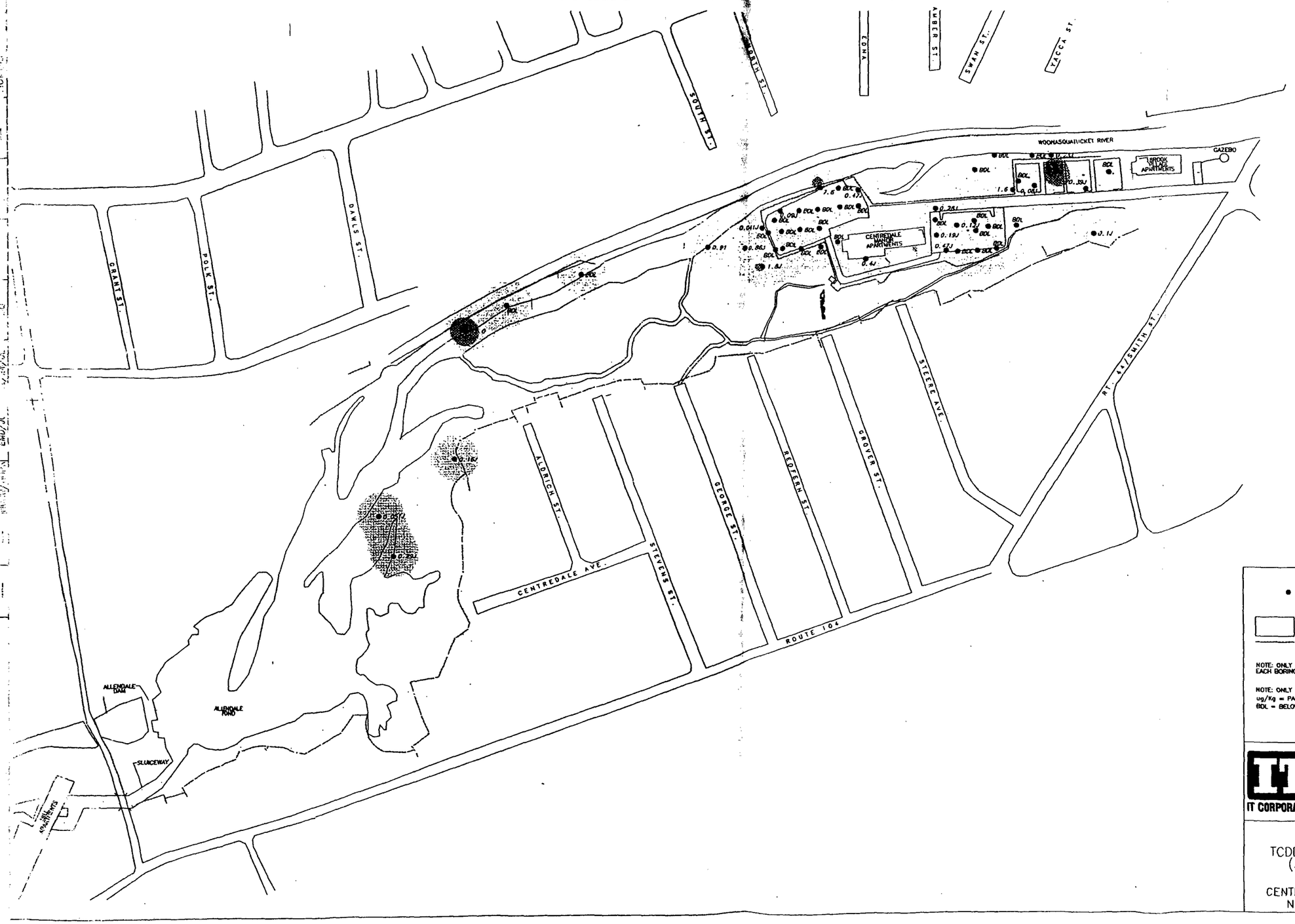
FIGURE 8c
TCDD Concentration Distribution in Soil
(2-3 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

TCDD Concentration Distribution in Soil
(3-4 feet below ground surface)
(June to November 1999)



Site Action Level

500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
0

Concentrations in micrograms per kilogram (ug/Kg)

LEGEND:

- SOIL BORING LOCATION
  1.6 - SAMPLE RESULT IN ug/Kg
- BUILDING OUTLINE
- FENCE

NOTE: ONLY THE MAXIMUM CONCENTRATION DETECTED IS LISTED FOR EACH BORING LOCATION.

NOTE: ONLY BORING LOCATIONS SAMPLED FOR DIOXIN ARE SHOWN.
ug/Kg = PARTS PER BILLION
BDL = BELOW DETECTION LIMIT

SCALE
0 125 250 375 FEET

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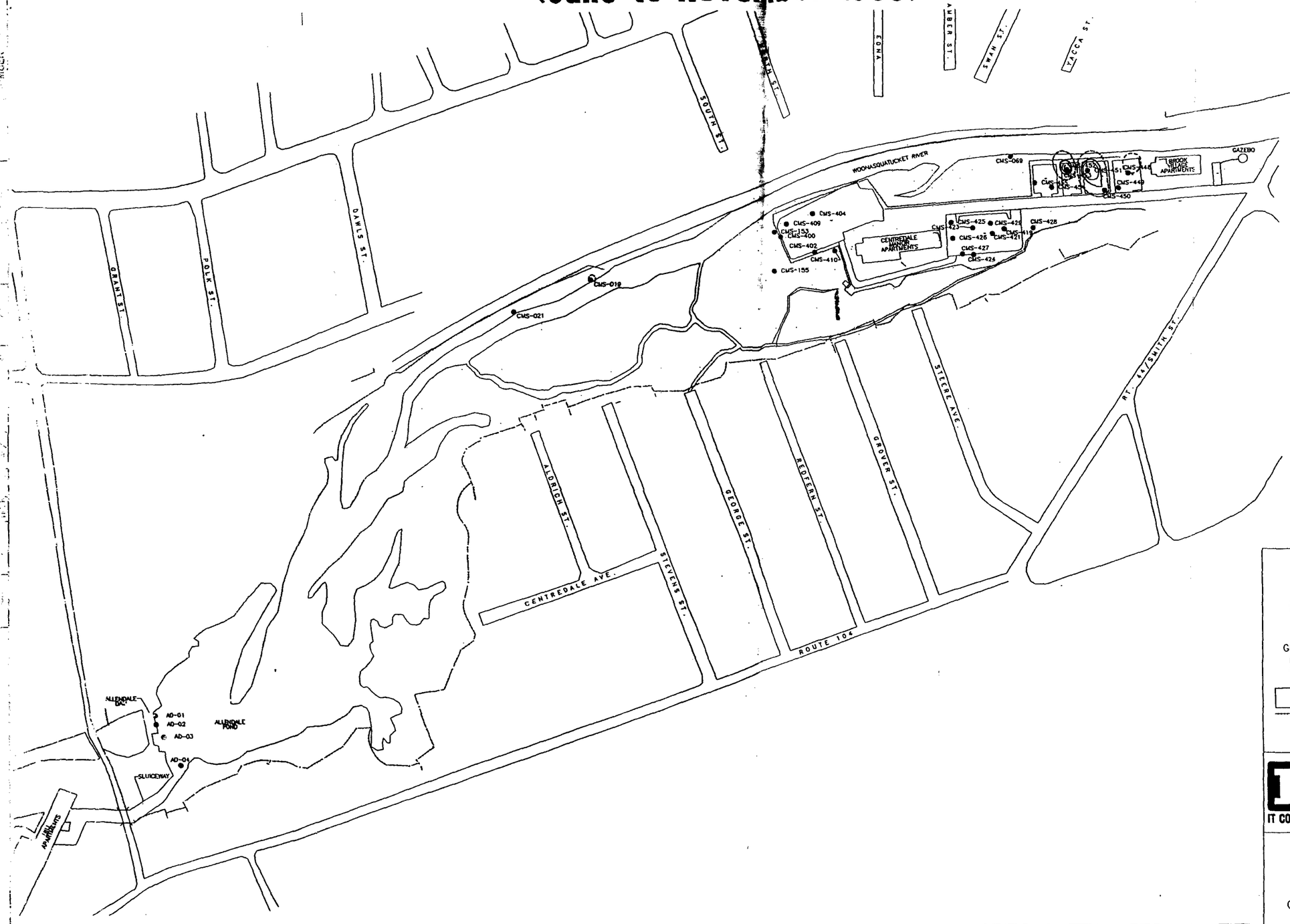
FIGURE 8d
TCDD Concentration Distribution in Soil
(3-4 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

TCDD Concentration Distribution in Soil
(4-8 feet below ground surface)
(June to November 1999)



LEGEND:

- SOIL BORING LOCATION
  EX.: CMS-155 - SOIL BORING IDENTIFICATION
- 1 ppb
- 5 pbb
- 10 ppb
- RED 4-5 FEET
- GREEN 5-6 FEET
- BLUE 6-7 FEET
- CYAN 7-8 FEET
- BUILDING OUTLINE
- FENCE

SCALE
0 125 250 375 FEET

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FIGURE 8e
TCDD Concentration Distribution in Soil
(4-8 feet below ground surface)
(June to November 1999)
CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

Dioxin/PCB
Concentration Summary Map
(February 1999 and June to November 1999)

TCDD
- BLANK = NO SAMPLE FOR TCDD
- ≥ 10ppb
- < 1ppb

PCBs
- BLANK = NO SAMPLE FOR PCBs
- ≥ 50ppm
- < 1ppm

* – LOCATION MOVED FOR CLARITY
LEADER DENOTES ACTUAL LOCATION

SCALE
0 125 250 375 FEET

SOUTH ST.
NORTH ST.
CONA
AMBER ST.
SWAN ST.
YACCA ST.
DAWLS ST.
GRANT ST.
POLK ST.
WOONASQUATUCKET RIVER
BROOK BLACK APARTMENTS
GAZEBO
CENTREDALE MANOR APARTMENTS
STEERE AVE.
RT. 44/SMITH ST.
ALDRICH ST.
GEORGE ST.
REDFERN ST.
GROVER ST.
CENTREDALE AVE.
STEVENS ST.
ROUTE 104
ALLENDALE DAM
ALLENDALE POND
SLUICEWAY
MILL No. 5

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FIGURE 9
Dioxin/PCB
Concentration Summary Map
(February 1999 and June to November 1999)

CENTREDALE MANOR RESTORATION PROJECT
NORTH PROVIDENCE, RHODE ISLAND

PLAINTIFF'S EXHIBIT 18 CLEARY - 2/10/03

State of California)
County of Mendocino) ss:

AFFIDAVIT OF THOMAS F. CLEARY

Thomas F. Cleary, being duly sworn, deposes and states as follows:

1. I have personal knowledge of the facts set forth in this affidavit and, if called as a witness, I could and would competently testify to the facts set forth below.

2. I am retired after a career working for several companies as an organic chemist.

3. I currently reside at 45451 S. Caspar Dr., Mendocino, CA 95460, phone 707-964-7065.

4. I have a B.S. in chemistry from Rutgers University.

5. Before my retirement, I was employed at Centerchem, Inc. between approximately 1960 to 1980 as an organic chemist and as President and Chief Executive Officer after 1977.

6. While working for Centerchem, Inc., I would solicit custom chemical manufacturing contracts for small chemical manufacturing companies.

7. As part of that work, I would assist the chemical manufacturers with development of the manufacturing processes used to fill their custom chemical manufacturing contracts.

8. In the 1960s I was acquainted with Metro-Atlantic, Inc., a chemical manufacturer located in North Providence, Rhode Island.

9. Metro-Atlantic was owned and run by Joseph Buonanno, now deceased.

10. I was acquainted with purchasing agents of Eli Lilly and Company of Indianapolis, IN and would attempt to assist in the development of contracts for the custom manufacture of chemicals for Eli Lilly by custom chemical manufacturing companies like Metro-Atlantic.

EXHIBIT 1

11. My primary contacts at Eli Lilly in the 1960s were Robert G. "Bob" Weigel, Eli Lilly's purchasing agent, now deceased, and assistant purchasing agent Robert Dille, also deceased.

12. In approximately 1963 or 1964, I became aware of Eli Lilly's development of a pesticide known as treflan or trifluralin.

13. When starting production of treflan, Eli Lilly needed time to design, build and start up the process equipment in its Tippecanoe, IN plant.

14. I suggested to Joseph Buonanno that Metro-Atlantic might be able to manufacture treflan for Eli Lilly.

15. I assisted Metro-Atlantic in developing the process to manufacture treflan at its North Providence, Rhode Island plant and Metro-Atlantic erected a building specifically to house that process at that time.

16. Eli Lilly entered into an agreement with Metro-Atlantic by which Metro-Atlantic made treflan for Eli Lilly at the Metro-Atlantic North Providence plant.

17. The treflan process at the North Providence plant consisted of converting the substrate parachlorobenzotrifluoride or PCBT, obtained from Hooker Chemical in Niagara Falls, N.Y., into treflan, first by dinitration then amination of the resulting 3,5-Dinitro-4-chlorobenzotifluoride with dipropylamine. The treflan active substance was formulated with solvents and emulsifiers supplied by and under the direction of Eli Lilly.

18. After a short period of production, no more than a few months at most, Eli Lilly began production of treflan at its Tippecanoe, IN plant and treflan production at the Metro-Atlantic North Providence, R.I. plant ceased.

19. The Metro-Atlantic production facility built for treflan production was not used for

some time after the treflan production ceased; I then worked with Joseph Buonanno to set up a process to manufacture hexachlorophene in the building formerly used to manufacture treflan.

20. The hexachlorophene produced by Metro-Atlantic was sold on the open market, with Sterling Winthrop being one of the largest purchasers.

21. To my knowledge, Eli Lilly had no relationship to the production of hexachlorophene at the Metro-Atlantic North Providence plant.

Further affiant sayeth not.

[name]

Subscribed to and sworn to before me this
8 day of ~~September~~ November, 2001.

My commission expires: 10-5-03

JACK R. DRUCKER
COMM. 1266608 - MEN. RCO
NOTARY PUBLIC
CALIFORNIA
MENDOCINO COUNTY
MY COMM. EXPIRES OCT. 5, 2003

DOCUMENTS TO BE PRODUCED

(1) any and all documents concerning the manufacture and/or sale of hexachlorophene by Metro-Atlantic, Inc, including any efforts to establish a process for such manufacture and/or sale of hexachlorophene, as referenced in paragraphs 19 and 20 of the affidavit of Thomas F. Cleary dated November 8, 2001 (a copy of which is attached), and (2) any and all documents concerning the chemical composition of the hexachlorophene manufactured and/or sold by Metro-Atlantic, Inc.

United States Patent Office

3,456,020

Patented July 15, 1969

3,456,020

PRODUCTION OF 2,2'-METHYLENE BIS(3,4,6-TRICHLOROPHENOL)

Thomas F. Cleary, Summit, N.J., assignor to Centerchem Inc., New York, N.Y., a corporation of New York

No Drawing. Continuation-in-part of application Ser. No. 489,036, Sept. 21, 1965. This application Nov. 28, 1967, Ser. No. 686,290

Int. Cl. C07c 37/00

U.S. Cl. 260—619 3 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to the production of hexachlorophene by a two stage process in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted under the influence of an acid catalyst, after which the reaction product is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid.

RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 489,036, now abandoned, filed Sept. 21, 1965, and having the same title as this application.

THE INVENTION

This invention relates generally to new and useful improvements for the production of 2,2'-methylene bis-(3,4,6-trichlorophenol), commonly called hexachlorophene, and particularly seeks to provide a novel two stage process for producing same.

The known processes for the preparation of hexachlorophene (2,2'-methylene bis(3,4,6-trichlorophenol)) involve the condensation of two mols of 2,4,5-trichlorophenol with one mol of formaldehyde (as Formalin or paraformaldehyde). The usual condensing agent is concentrated sulfuric acid or weak oleum, and the reaction may be carried out in the presence or absence of a solvent which is inert to the reactants and to the condensing agent.

In these processes it is customary to mix all of the reactants (and the solvent, if any) at once and to heat the mixture, with agitation, for a certain time. Conditions such as these are disadvantageous in the production of hexachlorophene in that:

(1) They tend to promote the formation of color bodies which make difficult the purification of the product;

(2) They tend to promote the formation of the by-product 2,4,5-trichlorobenzodioxolane with an attendant loss of yield;

(3) They require, if acceptable yields are to be obtained, extreme care that the 2,4,5-trichlorophenol and formaldehyde be present in exactly the molar ratio 2.00:1.00. Since the composition of Formalin or of formaldehyde is usually imprecise, and since a certain amount of formaldehyde is lost from the reaction mixture by volatilization, this is a difficult requirement to realize in practice.

However, through the use of this invention the above mentioned disadvantages in prior processes have been overcome.

Therefore, an object of this invention is to provide a new method of producing hexachlorophene from previously known source materials which is simpler, more effective and results in higher yields by comparison with prior processes.

Another object of this invention is to provide a process of the character stated in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted under the influence of an acidic catalyst to form a novel intermediate product, which in turn is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid to produce high yields of pure hexachlorophene.

With these and other objects, the nature of which will be apparent, the invention will be more fully understood by reference to the accompanying detailed description and the appended claims.

In accordance with this invention it has been discovered that:

(1) One mol of 2,4,5-trichlorophenol and one mol of formaldehyde will react, under the influence of acidic catalysts such as benzenesulfonic acid, anhydrous hydrogen, and diluted sulfuric acid, to form quantitatively and exclusively, a compound which has a melting point of 78° C. The compound has a chlorine content 46.5%, occurs in long colorless prisms, and definitely is not 2,4,5-trichlorosaligenin.

(2) The compound formed as in (1) can be condensed with 2,4,5-trichlorophenol, through the agency of chlorosulfonic acid or fluorosulfonic acid, to produce high yields of pure hexachlorophene.

Both of these reactions are surprising. The only hitherto known reaction product of equimolar amounts of 2,4,5-trichlorophenol and formaldehyde is 2,4,5-trichlorosaligenin, which is formed under alkaline conditions and has a melting point of 128° C. 2,4,5-trichlorophenol, which is relatively inert to concentrated sulfuric acid and to oleum, will react readily with chlorosulfonic acid and fluorosulfonic acid to form 2,4,5-trichlorophenol-6-sulfonic acid.

The following examples will illustrate this invention.

Example 1

197.5 grams of 2,4,5-trichlorophenol having a melting point of 66° C. is dissolved in 1000 grams of perchloroethylene and the solution is warmed to 50° C. with agitation. To this solution is added 50 grams of 90° sulfuric acid. 30 grams of paraformaldehyde is added slowly over a period of one hour with sufficient cooling to maintain the temperature between 60° C. and 70° C. The reaction is exothermic. The mixture is stirred for an additional two hours at 70° C. The perchloroethylene solution is then separated from the dilute acid layer. Upon evaporating a small sample to dryness a crystalline product is obtained which has a melting point of 78° C. There is no free formaldehyde remaining either in the dilute acid layer or in the perchloroethylene solution. There is no hexachlorophene present at this point in the reaction mixture, nor any unreacted 2,4,5-trichlorophenol.

The perchloroethylene solution of the product of the reaction between 2,4,5-trichlorophenol and paraformaldehyde is mixed with a solution of 197.5 grams of 2,4,5-trichlorophenol in 1000 grams of perchloroethylene and the mixture is heated with agitation to 75° C. There is then introduced dropwise over a period of three hours 116 grams of chlorosulfonic acid. The addition of chlorosulfonic acid is accompanied by a mild exothermic reaction and by the evolution of HCl. The temperature is maintained at 75° C. throughout the chlorosulfonic acid addition and is then held at 75° C. to 80° C. for an additional two hours. Agitation is stopped, the remaining sulfuric acid layer is allowed to settle and is separated. The hot perchloroethylene solution is stirred with 10 grams of activated charcoal and is filtered. The reaction product, 2,2'-methylene bis(3,4,6-trichlorophenol), crystallizes upon cooling and is separated by filtration. The yield is 310 grams having a melting point of 162° C. Upon concentration of the mother liquors there is obtained an additional 65 grams of product having the same melting point.

Example 2

197.5 grams of 2,4,5-trichlorophenol having a melting point of 62° C. is dissolved in 2000 ml. of chloroform, and the solution is warmed to 50° C. with agitation. Dry hydrogen chloride is bubbled through the solution at a rate of 5 grams per minute, and over a period of one hour, 31.6 grams of 95% paraformaldehyde is added. Hydrogen chloride addition is continued for 30 minutes, and the mixture is then heated to reflux for one hour.

A small sample of the reaction mixture, evaporated to dryness, yields a white crystalline compound, having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

To the reaction mixture is then added a solution of 197.5 grams of 2,4,5-trichlorophenol, having a melting point of 62° C., in 2000 ml. of chloroform. The mixture is heated to 65° C., under a reflux condenser and with good agitation, 100 grams of fluorosulfonic acid is added dropwise, over a period of three hours. Agitation and heating at 65° C. are continued for three hours more, then agitation is stopped, the acid layer is settled and separated. The hot chloroform solution is stirred with 10 grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold chloroform and dried. The yield is 310 grams having a melting point of 164° C. Evaporation of the mother liquor yields an additional 70 grams of product.

Example 3

To 1000 ml. of benzene is added, slowly, 58 grams of chlorosulfonic acid, and the solution is then heated to reflux until all HCl is driven off. There is thus produced a benzene solution containing 79 grams benzenesulfonic acid. To this solution is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is then heated just to the point of reflux, and with good agitation, 85 grams of 37% Formalin is added over two hours, while the water introduced with the Formalin is taken off as an azeotrope with benzene. The condensed benzene is returned to the reaction mixture. Reflux is then continued for one hour, after which 500 ml. of water is added. The mixture stirred 15 minutes at 60° C., and settled. The water layer which contains the benzenesulfonic acid, is separated and discarded.

A small sample of the benzene solution evaporated to dryness, yields a white crystalline product having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

The benzene solution is added to 2000 ml. of perchloroethylene, and the benzene is removed from the mixture by fractional distillation.

To the remaining perchloroethylene solution of the reaction product of 2,4,5-trichlorophenol with Formalin is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is heated to 75° C., and with vigorous agitation is added, over five hours, 116 grams chlorosulfonic acid. Stirring is continued at 75° C. for two hours and the acid layer is then settled and separated. The hot perchloroethylene solution is stirred with ten grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold perchloroethylene and dried. The yield is 280 grams having a melting point of 163° C. Evaporation of the mother liquor yields an additional 85 grams of product.

I claim:

1. In a method for producing hexachlorophene the steps of, supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the pressure of an acid catalyst selected from the group consisting of benzene-sulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid to form a solution of a compound which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%, then adding a solution of 1 mol of 2,4,5-trichlorophenol to the solution containing the reaction product of the preceding step, and effecting condensation therebetween by the addition of a sulfonic acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid to produce pure hexachlorophene.

2. A reaction product between 2,4,5-trichlorophenol and formaldehyde, having a melting point of 78° C. and a chlorine content of 46.5%, produced by supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the presence of an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid, and separating the solvent solution containing the reaction product from the acid.

3. In a method for producing hexachlorophene the steps of; dissolving a molar equivalent of 2,4,5-trichlorophenol in a solvent selected from the group consisting of perchlorethylene, chloroform and benzene; adding to said solution an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid; then adding a molar equivalent of formaldehyde and maintaining the temperature between about 60° C. and about 70° C. during the exothermic reaction produced as the result of such addition to produce a reaction product which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%; separating the solvent solution from the acid; adding a molar equivalent of 2,4,5-trichlorophenol dissolved in said solvent to said separated solvent solution; effecting condensation between said added molar equivalent of said 2,4,5-trichlorophenol and the reaction product in said separated solvent solution by the addition of an acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid; then removing the solvent solution containing the condensed product and recovering pure hexachlorophene therefrom by cooling and filtering same.

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LEON ZITVER, Primary Examiner

N. MORGENSTERN, Assistant Examiner

United States Patent Office

3,499,045
Patented Mar. 3, 1970

3,499,045

PURIFICATION OF 2,4,5-TRICHLOROPHENOL

Thomas F. Cleary, Summit, N.J., assignor to Centerchem, Inc., New York, N.Y., a corporation of New York

No Drawing. Filed Oct. 20, 1966, Ser. No. 587,991
Int. Cl. C07c 39/32
U.S. Cl. 260—623 1 Claim

ABSTRACT OF THE DISCLOSURE

This invention is directed to a method for purifying crude 2,4,5-trichlorophenol by treating it with an aqueous alkali hydroxide to form an alkali salt of the crude product, adding an additional quantity of the alkali hydroxide, then crystallizing and separating the alkali salt of 2,4,5-trichlorophenol and recovering essentially pure 2,4,5-trichlorophenol from the separated alkali salt by treating the salt with an acid.

This invention relates to new and useful improvements in the production of essentially pure 2,4,5-trichlorophenol and particularly seeks to provide a novel method for purifying crude 2,4,5-trichlorophenol.

2,4,5-trichlorophenol is produced conventionally by the reaction of 1,2,4,5-tetrachlorobenzene with methyl alcoholic or aqueous methyl alcoholic sodium hydroxide at an elevated temperature and pressure. The resulting crude product when isolated contains only about 88–92% of the desired 2,4,5-trichlorophenol and is inevitably accompanied by at least three impurities consisting of the methyl ether of 2,4,5-trichlorophenol, the 2,4-5-trichlorophenyl ether of 2,4,5-trichlorophenol, and 2,4-dichlorophenol. The latter impurity results from trichlorobenzene which is present as an impurity in the tetrachlorobenzene. There are also traces of several other impurities which occur as by-products or as substances present in the starting reactants.

Heretofore a degree of purification has been effected in a costly manner by a single distillation which raises the 2,4,5-trichlorophenol content to about 94–96% while a second distillation will raise it only slightly more to about 97–98% and even this degree of purity is inadequate for certain end uses. Furthermore, the yield of purified 2,4,5-trichlorophenol obtained by distillation is not very high because a very careful fractionation must be carried out.

However, in accordance with this invention it is possible to simply and inexpensively separate essentially pure 2,4,5-trichlorophenol from the crude reaction mixture.

Therefore, an object of this invention is to provide a novel process for purifying 2,4,5-trichlorophenol.

Another object of this invention is to provide a process of the character stated in which at least 95% of the 2,4,5-trichlorophenol present in the crude product is recovered in at least a 99.5% pure state and has a melting point of 65 to 67° C.

Another object of this invention is to provide a process of the character stated that is based upon the separation of 2,4,5-trichlorophenol from an aqueous medium as its sodium or potassium salt, in the presence of an excess of an alkali hydroxide, followed by liberation of free 2,4,5-trichlorophenol by acidification of the salt.

The following examples are illustrative of the invention:

EXAMPLE I

200 grams of a commercial grade of 2,4,5-trichlorophenol containing 94% of the 2.4,5-isomer was dissolved in 600 grams of 10% sodium hydroxide solution, and this solution was heated to 60° C. Any insoluble matter which was apparent in this solution was filtered off and there

was then added 600 grams of 50% sodium hydroxide solution, and the mixture was stirred while external cooling was applied. Over a period of 3 hours the mixture was cooled to 15° C., whereupon a heavy crystal mass of the sodium salt of 2,4,5-trichlorophenol had formed. The crystals were filtered off and washed with a small quantity of cold 30% sodium hydroxide solution. The pure white crystals were dissolved in 2 liters of water, and with stirring and cooling, the solution was adjusted to a pH of 3.0 with dilute hydrochloric acid. The 2,4,5-trichlorophenol which precipitated, was filtered off, washed with water, and dried. The yield of purified 2,4,5-trichlorophenol, having an assay of 99.6% and a melting point of 65.5 C. was 179 grams, representing a recovery of 95% of the 2,4,5-trichlorophenol which was present in the starting crude material.

EXAMPLE II

430 grams of commercial grade 1,2,4,5-tetrachlorobenzene was dissolved in 1,000 cc. of methyl alcohol, and 400 grams of 50% sodium hydroxide solution was added. This mixture was heated in an autoclave at 160° for 6 hours. The reaction mixture was then cooled to 30° C., and 500 cc. of water was added. The methyl alcohol was then distilled off and the residue was subjected to steam distillation until no organic matter was evident in the steam distillate. To the residue was then added 1,200 grams of 50% sodium hydroxide solution and the entire mixture was heated to 60° C. An additional 500 cc. of water was added, and the mixture was cooled over a period of 6 hours to 15° C., whereupon a heavy crystal mass of the sodium salt of 2,4,5-trichlorophenol formed. The crystals were removed by filtration, and washed with a small quantity of cold 30% sodium hydroxide solution. The crystals were dissolved in 1 liter of water and the solution was warmed to 70° C., and acidified to pH 3 with dilute hydrochloric acid. The 2,4,5-trichlorophenol separated from the warm mixture as an oil, and was removed from the water layer. The product had a setting point of 65° C., and an assay of 99.5% 2,4,5-trichlorophenol. The yield was 320 grams which represents a yield of 80.8% of the theoretical amount of pure 2,4,5-trichlorophenol from 1,2,4,5-tetrachlorobenzene.

EXAMPLE III

200 grams of a crude technical grade of 2,4,5-trichlorophenol, having an assay of 92.5% of the 2,4,5-isomer is dissolved in 600 cc. of 10% potassium hydroxide solution. The solution is heated to 60° C., and 800 grams of 50% potassium hydroxide solution is added. The mixture is cooled with stirring over a period of 8 hours to 12° C. The formed crystals of the potassium salt of 2,4,5-trichlorophenol are filtered off and washed with a small quantity of cold 25% potassium hydroxide solution. The crystals are dissolved in 1 liter of water, and 300 cc. of chloroform is added. With stirring, the mixture is acidified to a pH of 2.0 with dilute sulfuric acid. The chloroform solution is separated and clarified by filtration. The chloroform is distilled off, leaving a residue of 177 grams of 2,4,5-trichlorophenol having an assay of 99.7%, and a melting point of 66.5° C. This represents a recovery of 95% of the 2,4,5-trichlorophenol which was present in the crude starting material.

In the foregoing examples the excess alkali hydroxide should be present in an amount ranging from 1 to 3 times the weight of the 2,4,5-trichlorophenol.

Although only hydrochloric and sulfuric acids have been disclosed as the acidifying agents, it will be appreciated that many other acids could be used for this purpose as long as they are capable of reducing the pH to 4.5 or lower.

The phrase "essentially pure" is intended to indicate a purity of at least 99.5%.

I claim:

1. In a process for obtaining essentially pure 2,4,5-trichlorophenol from a crude product, wherein the crude product is obtained from the hydrolysis of 1,2,4,5-tetrachlorobenzene, the steps of forming an alkali salt of 2,4,5-trichlorophenol by treating said crude product with an aqueous alkali hydroxide selected from the group consisting of sodium and potassium hydroxides in which an excess of said alkali hydroxide is added at the ratio of about 1 to 3 weight units for each weight unit of 2,4,5-trichlorophenol present, cooling to crystallize said alkali salt and thereafter separating the said crystalized alkali salt of 2,4,5-trichlorophenol from solution by filtration, and recovering 2,4,5-trichlorophenol from the said alkali salt thereof by treating said alkali salt with an acid selected from the group consisting of hydrochloric and sulfuric acid.

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BERNARD HELFIN, Primary Examiner

W. B. LONE, Assistant Examiner

United States Patent Office 3,456,020 Patented July 15, 1969

3,456,020
PRODUCTION OF 2,2'-METHYLENE BIS(3,4,6-TRICHLOROPHENOL)

Thomas F. Cleary, Summit, N.J., assignor to Centerchem Inc., New York, N.Y., a corporation of New York

No Drawing. Continuation-in-part of application Ser. No. 489,036, Sept. 21, 1965. This application Nov. 28, 1967, Ser. No. 686,290

Int. Cl. C07c 37/00

U.S. Cl. 260—619 3 Claims

ABSTRACT OF THE DISCLOSURE

This invention is directed to the production of hexachlorophene by a two stage process in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted under the influence of an acid catalyst, after which the reaction product is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid.

RELATED APPLICATION

This application is a continuation-in-part of my copending application Ser. No. 489,036, now abandoned, filed Sept. 21, 1965, and having the same title as this application.

THE INVENTION

This invention relates generally to new and useful improvements for the production of 2,2'-methylene bis-(3,4,6-trichlorophenol), commonly called hexachlorophene, and particularly seeks to provide a novel two stage process for producing same.

The known processes for the preparation of hexachlorophene (2,2'-methylene bis(3,4,6-trichlorophenol)) involve the condensation of two mols of 2,4,5-trichlorophenol with one mol of formaldehyde (as Formalin or paraformaldehyde). The usual condensing agent is concentrated sulfuric acid or weak oleum, and the reaction may be carried out in the presence or absence of a solvent which is inert to the reactants and to the condensing agent.

In these processes it is customary to mix all of the reactants (and the solvent, if any) at once and to heat the mixture, with agitation, for a certain time. Conditions such as these are disadvantageous in the production of hexachlorophene in that:

(1) They tend to promote the formation of color bodies which make difficult the purification of the product;

(2) They tend to promote the formation of the by-product 2,4,5-trichlorobenzodioxolane with an attendant loss of yield;

(3) They require, if acceptable yields are to be obtained, extreme care that the 2,4,5-trichlorophenol and formaldehyde be present in exactly the molar ratio 2.00:1.00. Since the composition of Formalin or of formaldehyde is usually imprecise, and since a certain amount of formaldehyde is lost from the reaction mixture by volatilization, this is a difficult requirement to realize in practice.

However, through the use of this invention the above mentioned disadvantages in prior processes have been overcome.

Therefore, an object of this invention is to provide a new method of producing hexachlorophene from previously known source materials which is simpler, more effective and results in higher yields by comparison with prior processes.

Another object of this invention is to provide a process of the character stated in which one mol of 2,4,5-trichlorophenol and one mol of formaldehyde are reacted

under the influence of an acidic catalyst to form a novel intermediate product, which in turn is condensed with one mol of 2,4,5-trichlorophenol through the agency of chlorosulfonic acid or fluorosulfonic acid to produce high yields of pure hexachlorophene.

With these and other objects, the nature of which will be apparent, the invention will be more fully understood by reference to the accompanying detailed description and the appended claims.

In accordance with this invention it has been discovered that:

(1) One mol of 2,4,5-trichlorophenol and one mol of formaldehyde will react, under the influence of acidic catalysts such as benzenesulfonic acid, anhydrous hydrogen, and diluted sulfuric acid, to form quantitatively and exclusively, a compound which has a melting point of 78° C. The compound has a chlorine content 46.5%, occurs in long colorless prisms, and definitely is not 2,4,5-trichlorosaligenin.

(2) The compound formed as in (1) can be condensed with 2,4,5-trichlorophenol, through the agency of chlorosulfonic acid or fluorosulfonic acid, to produce high yields of pure hexachlorophene.

Both of these reactions are surprising. The only hitherto known reaction product of equimolar amounts of 2,4,5-trichlorophenol and formaldehyde is 2,4,5-trichlorosaligenin, which is formed under alkaline conditions and has a melting point of 128° C. 2,4,5-trichlorophenol, which is relatively inert to concentrated sulfuric acid and to oleum, will react readily with chlorosulfonic acid and fluorosulfonic acid to form 2,4,5-trichlorophenol-6-sulfonic acid.

The following examples will illustrate this invention.

Example 1

197.5 grams of 2,4,5-trichlorophenol having a melting point of 66° C. is dissolved in 1000 grams of perchloroethylene and the solution is warmed to 50° C. with agitation. To this solution is added 50 grams of 90° sulfuric acid. 30 grams of paraformaldehyde is added slowly over a period of one hour with sufficient cooling to maintain the temperature between 60° C. and 70° C. The reaction is exothermic. The mixture is stirred for an additional two hours at 70° C. The perchloroethylene solution is then separated from the dilute acid layer. Upon evaporating a small sample to dryness a crystalline product is obtained which has a melting point of 78° C. There is no free formaldehyde remaining either in the dilute acid layer or in the perchloroethylene solution. There is no hexachlorophene present at this point in the reaction mixture, nor any unreacted 2,4,5-trichlorophenol.

The perchloroethylene solution of the product of the reaction between 2,4,5-trichlorophenol and paraformaldehyde is mixed with a solution of 197.5 grams of 2,4,5-trichlorophenol in 1000 grams of perchloroethylene and the mixture is heated with agitation to 75° C. There is then introduced dropwise over a period of three hours 116 grams of chlorosulfonic acid. The addition of chlorosulfonic acid is accompanied by a mild exothermic reaction and by the evolution of HCl. The temperature is maintained at 75° C. throughout the chlorosulfonic acid addition and is then held at 75° C. to 80° C. for an additional two hours. Agitation is stopped, the remaining sulfuric acid layer is allowed to settle and is separated. The hot perchloroethylene solution is stirred with 10 grams of activated charcoal and is filtered. The reaction product, 2,2'-methylene bis(3,4,6-trichlorophenol), crystallizes upon cooling and is separated by filtration. The yield is 310 grams having a melting point of 162° C. Upon concentration of the mother liquors there is obtained an additional 65 grams of product having the same melting point.

Example 2

197.5 grams of 2,4,5-trichlorophenol having a melting point of 62° C. is dissolved in 2000 ml. of chloroform, and the solution is warmed to 50° C. with agitation. Dry hydrogen chloride is bubbled through the solution at a rate of 5 grams per minute, and over a period of one hour, 31.6 grams of 95% paraformaldehyde is added. Hydrogen chloride addition is continued for 30 minutes, and the mixture is then heated to reflux for one hour.

A small sample of the reaction mixture, evaporated to dryness, yields a white crystalline compound, having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

To the reaction mixture is then added a solution of 197.5 grams of 2,4,5-trichlorophenol, having a melting point of 62° C., in 2000 ml. of chloroform. The mixture is heated to 65° C., under a reflux condenser and with good agitation, 100 grams of fluorosulfonic acid is added dropwise, over a period of three hours. Agitation and heating at 65° C. are continued for three hours more, then agitation is stopped, the acid layer is settled and separated. The hot chloroform solution is stirred with 10 grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold chloroform and dried. The yield is 310 grams having a melting point of 164° C. Evaporation of the mother liquor yields an additional 70 grams of product.

Example 3

To 1000 ml. of benzene is added, slowly, 58 grams of chlorosulfonic acid, and the solution is then heated to reflux until all HCl is driven off. There is thus produced a benzene solution containing 79 grams benzenesulfonic acid. To this solution is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is then heated just to the point of reflux, and with good agitation, 85 grams of 37% Formalin is added over two hours, while the water introduced with the Formalin is taken off as an azeotrope with benzene. The condensed benzene is returned to the reaction mixture. Reflux is then continued for one hour, after which 500 ml. of water is added. The mixture stirred 15 minutes at 60° C., and settled. The water layer which contains the benzenesulfonic acid, is separated and discarded.

A small sample of the benzene solution evaporated to dryness, yields a white crystalline product having a melting point of 78° C. It contains no 2,4,5-trichlorophenol or formaldehyde.

The benzene solution is added to 2000 ml. of perchloroethylene, and the benzene is removed from the mixture by fractional distillation.

To the remaining perchloroethylene solution of the reaction product of 2,4,5-trichlorophenol with Formalin is added 197.5 grams 2,4,5-trichlorophenol having a melting point of 62° C. The solution is heated to 75° C., and with vigorous agitation is added, over five hours, 116 grams chlorosulfonic acid. Stirring is continued at 75° C. for two hours and the acid layer is then settled and separated. The hot perchloroethylene solution is stirred with ten grams activated charcoal, filtered and cooled to 10° C. The crystallized 2,2'-methylene bis(3,4,6-trichlorophenol) is filtered off, washed with cold perchloroethylene and dried. The yield is 280 grams having a melting point of 163° C. Evaporation of the mother liquor yields an additional 85 grams of product.

I claim:

1. In a method for producing hexachlorophene the steps of, supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the pressure of an acid catalyst selected from the group consisting of benzene-sulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid to form a solution of a compound which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%, then adding a solution of 1 mol of 2,4,5-trichlorophenol to the solution containing the reaction product of the preceding step, and effecting condensation therebetween by the addition of a sulfonic acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid to produce pure hexachlorophene.

2. A reaction product between 2,4,5-trichlorophenol and formaldehyde, having a melting point of 78° C. and a chlorine content of 46.5%, produced by supplying a solution of 2,4,5-trichlorophenol and formaldehyde at a 1 to 1 molar ratio in a solvent selected from the group consisting of perchloroethylene, chloroform and benzene, reacting said 2,4,5-trichlorophenol and formaldehyde in the presence of an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid, and separating the solvent solution containing the reaction product from the acid.

3. In a method for producing hexachlorophene the steps of; dissolving a molar equivalent of 2,4,5-trichlorophenol in a solvent selected from the group consisting of perchlorethylene, chloroform and benzene; adding to said solution an acid catalyst selected from the group consisting of benzenesulfonic acid, anhydrous hydrogen chloride and diluted sulfuric acid; then adding a molar equivalent of formaldehyde and maintaining the temperature between about 60° C. and about 70° C. during the exothermic reaction produced as the result of such addition to produce a reaction product which, when dry, has a melting point of 78° C. and a chlorine content of 46.5%; separating the solvent solution from the acid; adding a molar equivalent of 2,4,5-trichlorophenol dissolved in said solvent to said separated solvent solution; effecting condensation between said added molar equivalent of said 2,4,5-trichlorophenol and the reaction product in said separated solvent solution by the addition of an acid selected from the group consisting of chlorosulfonic acid and fluorosulfonic acid; then removing the solvent solution containing the condensed product and recovering pure hexachlorophene therefrom by cooling and filtering same.

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LEON ZITVER, Primary Examiner

N. MORGENSTERN, Assistant Examiner

ERRATUM

SPECIFICATION No. 1,016,080
Amendment No. 1

Page 4, Table 1, Column 8, *line* $\frac{CH_3OH}{TcB}$

for "$\frac{12.5}{1}$" *read* "$\frac{11}{1}$"

THE PATENT OFFICE
3rd October 1966

1,016,080

PATENT SPECIFICATION

NO DRAWINGS

1,016,080

Date of Application and filing Complete Specification: May 17, 1963.

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COMPLETE SPECIFICATION

Improvements in or relating to Alkali Metal Polyhalo-Phenates

We, DIAMOND ALKALI COMPANY, of 300 Union Commerce Building, Cleveland 14, Ohio, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, (Assignees of JEWEL HEBER PERKINS, Jr., JACK A. BORROR and RAYMOND AUGUST GUIDI) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new and improved method of preparing polyhalophenates, and more specifically refers to improvements in the preparation of sodium 2,4,5-trichlorophenate.

Polyhalophenates, such as sodium 2,4,5-trichlorophenates, are used as raw materials in the production of polyhalophenoxycarboxylic acids which are widely used as herbicides, and there has been a continuing desire to produce such starting materials economically, safely and efficiently.

Referring particularly to the preparation of sodium 2,4,5-trichlorophenate as an illustration, it is known to prepare this material by reacting molten tetrachlorobenzene with a mixture of sodium hydroxide and methanol or water or glycol, by adding all the reactants together as a charge to a reaction vessel, then heating them under pressure to 100°—250° C. to produce the required reactions. This method involves a danger due to the creation of conditions causing runaway reactions and the formation of chloracnegens, and is generally less efficient than the method of this invention. The known method requires the heating of a large amount of a caustic-tetrachlorobenzene mixture which may result in condensation reactions, causing a reduction in efficiency.

It is an object of the present invention to provide an improved method of producing a polyhalophenate, notably sodium 2,4,5-trichlorophenate, in high yield, in a manner which avoids the hazardous condition of reacting large amounts of hot alkali and alcohol with tetrachlorobenzene.

According to the invention, an alkali metal polyhalophenate is prepared by heating a 1,2,4,5-tetrahalobenzene in a closed vessel to a temperature in the range of 140° to 250° C., adding a mixture of an alcohol and an alkali metal hydroxide at a controlled rate, the mol ratio of alcohol to alkali metal hydroxide being from 2:1 to 20:1, and maintaining the reaction temperature in the range of 140° to 250° C. under a superatmospheric pressure which is at least equal to the autogenous pressure of the reaction mixture, the amount of alcohol-alkali mixture being such as to provide a mol ratio of alkali to tetrahalobenzene of from 2:1 to 4:1.

The desired reaction product is obtained in high yield and, at the same time, the undesired dangerous condition of large quantities of unreacted tetrachlorobenzene and alkali-alcohol mixture together in a pressurized high-temperature container is avoided.

The terms "polyhalophenate" and "tetrahalobenzene" refer respectively to various halogen derivatives of phenol, such as tetrachlorophenol, and of benzene. While chlorine derivatives are preferred, other halogen derivatives are contemplated such as bromo, fluoro, iodo; and mixed halogen products such as bromochlorophenol.

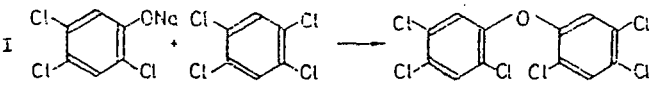
The term "alkali", as used in the specification, refers especially to an alkali metal hydroxide, preferably sodium hydroxide, although other alkali metal hydroxides, e.g., potassium hydroxide and/or lithium hydroxide can be used. It is intended to refer

also to other sources of alkali, which, under the conditions of reaction, are suitable to yield the desired high conversion characterizing the practice of this invention, and otherwise to be satisfactory. An alkali metal hydroxide, notably sodium hydroxide, is especially preferred.

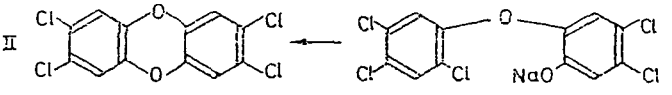
The term "alcohol" means primary, secondary and tertiary alcohols. Methanol is the preferred alcohol.

It is an essential feature of the present invention that a polyhalobenzene, preferably tetrachlorobenzene, is placed in a reaction vessel in a molten or solid state in the absence of any other reactants. The desired reaction is then carried out by the gradual addition of an alkali in alcohol mixture to the molten tetrachlorobenzene. The addition, at a controllable rate, is seen to be inherently safer than adding all the reactants at once and heating the mass to the relatively high temperatures required for the reaction. Another significant advantage of this invention is that less alkali is required. Previous methods require 3.0 mol of alkali per mol of tetrachlorobenzene. The proposed process provides nearly 100% yield at 2.4 mol of alkali per mol of tetrachlorobenzene. Formerly, large amounts of alkali present caused the following condensation reactions which resulted in a corresponding loss of the product and reduction in efficiency.

I



II



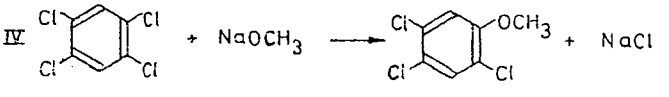
This undesirable condition is minimized by the controlled addition of small quantities of alkali-alcohol mixtures. The end product of the above reactions is termed a "chloracnegen". Condensation products of this class create the occupational hazard of skin disease known to those employed in the art as "chlor-acne". This disorder has been prevalent among operators of prior processes and the absence of the "chloracnegen" renders the method of this invention more desirable than previous processes.

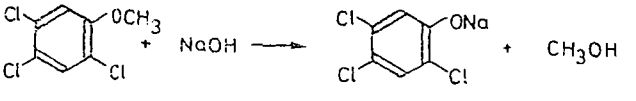
In previous processes, large quantities of alcohol, present in the reaction vessel at the start of the reaction, are subjected to high temperatures before the reaction can be completed, resulting in losses through formation of dimethyl ether. The controlled addition of alkali-alcohol mixture to the reaction vessel, in accordance with the teachings of this invention, reduces losses in alcohol by formation of dimethyl ether by-product.

The sequence of reaction steps of this invention is set forth structurally in the following series of equations, it being understood that the alkali-alcohol mixture is added at a rate pre-determined to produce the most efficient reaction possible. It will then be appreciated that the reaction proceeds only as the reactants become available in the reaction vessel.

III $NaOH + CH_3OH \rightleftharpoons NaOCH_3 + H_2O$

IV





With the practice of the invention, as outlined in the foregoing equations, conversion of greater than 90% of 1,2,4,5-tetrachlorobenzene to sodium 2,4,5-trichlorophenate is obtained. The reaction temperature varies from 140° C. to 250° C., preferably maintained at 175° C. and a superatmospheric pressure is provided which is at least equal to the autogenous pressure of the reaction mixture. The reaction time typically is 3 to 6 hours, although in commercial operations a longer reaction time of up to 8 hours is not disadvantageous with respect to high yields obtained.

The proportions of the reactants generally can be varied. Thus, molar ratios in the alkali-alcohol mix can be from 1:2 to 1:20 mols of alkali to alcohol. The overall molar ratios of alkali to tetrachlorobenzene can be from 2:1 to 4:1. The overall molar ratios of alcohol to tetrachlorobenzene can be in the range of 4:1 to 80:1. It is the preferred method to add 2.04 pounds of alkali-alcohol solution per pound of 1,2,4,5-tetrachlorobenzene into the reactor at a uniform rate over a period of 2 hours, maintaining the temperature at approximately 175° C. Steel equipment is employed in the examples of this invention, and steel is the preferred material of construction.

In order that those skilled in the art may more completely understand the present invention and the preferred method by which the same may be carried into effect, the following specific examples are offered.

Tetrachlorobenzene is weighed into a pressure reactor, such as an autoclave, melted and brought up to the reaction temperature, e.g., 175° C. An alkali methanol solution is heated to 55°—65° C. and added to the reactor over a period which may vary from 40 minutes to 5 hours, preferably at a controlled rate of addition which is within the range of 0.4 to 11 mol per hour. When all of the alkali methanol solution has been charged, the reactor temperature is held constant, e.g. at 175° C., for a period which may vary from 40 minutes to 3 hours. During the reaction, the pressure within the reactor will be in the range of 250 p.s.i.g. to 700 p.s.i.g., due to the autogenous pressure of the alcohol, and will vary according to the amount of alcohol added. When the reaction is complete, the charge is cooled to reduce pressure. Steam is applied to the reaction vessel to distill off all the unreacted methanol which is collected through a condenser system and recovered. When all the methanol has been removed, water is added to the reaction mass which is now a crude sodium trichlorophenate. The crude sodium trichlorophenate is transferred to a distillation vessel, where by steam distillation the intermediate reaction product, trichloroanisole, is removed and recovered. The steam-stripped sodium trichlorophenate is then pumped through an enclosed filter, which removes the salts, and is then diluted and stored for later use in the 2,4,5-trichlorophenoxyacetic acid production.

By way of illustration, the process of the invention is carried out by heating 1,2,4,5-tetrachlorobenzene in the closed reaction vessel to a temperature of 175° C., adding 11 mol per hour of sodium hydroxide contained in a mixture with methanol, the mol ratio of methanol to sodium hydroxide being 5.4:1, and maintaining the reaction temperature of 175° C. for a period of 3 hours, under a pressure of 270 to 490 p.s.i.g., the amount of methanol sodium hydroxide mixture being such as to provide a mol ratio of sodium hydroxide to tetrachlorobenzene of about 2.2:1.

In the following examples, carried out in the manner indicated, the results are indexed comparatively:

TABLE I

	1	2	3	4	5	6	7	8	9	10	11	12	13
Mole Ratio													
$\frac{NaOH}{CH_3OH}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$	$\frac{1}{5}$
$\frac{NaOH}{TCB^*}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.5}{1}$	$\frac{2.5}{1}$	$\frac{2.5}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$	$\frac{2.2}{1}$
$\frac{CH_3OH}{TCB^*}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{12.5}{1}$	$\frac{12.5}{1}$	$\frac{12.5}{1}$	$\frac{12.5}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$	$\frac{11}{1}$
Conditions													
% Excess NaOH	10	10	10	10	25	25	25	10	10	10	10	10	10
Total charge gm.	3280	3280	3280	3280	3580	3580	3580	3280	3280	3280	3280	3280	3280
Feed Time (hrs.)	2	5	2	3	5	3	4	2	2	2	2	1	¾
Hold Time (hrs.)	2	½	1	1	1	1	1	2	3	1	2	2	3
Reaction Temp., °C.	140—72	165—68	164—65	165	164—66	163—64	163—64	157—62	163—64	174—75	170—88	164—67	173—79
% Conversion to sodium Trichlorophenate	72.2	73.9	89.3	74.5	90.0	85.7	83.3	82.7	92.7	90.2	96.0	89.9	96.8
Maximum Pressure PSIG	340	225	305	360	565	400	280	265	320	420	330	370	385

* 1,2,4,5-tetrachlorobenzene

EXAMPLE 14.

To the reaction vessel is added 1,080 g. (5 mol) of 1,2,4,5-tetrachlorobenzene. A 20% by weight NaOH in methanol solution is prepared by adding 440 g. (11 mol) NaOH pellets to 1,920 g. (60 mol) of commercial grade methanol and heated to 63° C. The reaction vessel is heated to 170° C., at which time the alkali methanol mixture is added to the reaction vessel over a period of 1 hour at a uniform rate, which will ultimately provide a 2.2:1 mol ratio of alkali to tetrachlorobenzene, respectively. At the end of 1 hour, when all the alkali methanol mixture has been added, the closed reaction vessel is maintained at 175° C. for a period of 3 hours. The pressure within the container reaches a maximum of 492 p.s.i.g. approximately one hour after the end of the alkali methanol addition. After cooling, pressure is reduced, and steam is applied to the reaction vessel to distill off the unreacted methanol. When all the methanol has been removed, water is added, and the crude sodium trichlorophenate may be purified if desired.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the full intended scope of this invention, as defined by the appended claims.

WHAT WE CLAIM IS:—

1. A process of preparing an alkali metal polyhalophenate, which comprises heating a 1,2,4,5-tetrahalobenzene in a closed vessel to a temperature in the range of 140° to 250° C., adding a mixture of an alcohol and an alkali metal hydroxide at a controlled rate, the mol ratio of alcohol to alkali metal hydroxide being from 2:1 to 20:1, and maintaining the reaction temperature in the range of 140° to 250° C. under a superatmospheric pressure which is at least equal to the autogenous pressure of the reaction mixture, the amount of alcohol-alkali mixture being such as to provide a mol ratio of alkali to tetrahalobenzene of from 2:1 to 4:1.

2. A process as claimed in Claim 1, wherein the tetrahalobenzene is 1,2,4,5-tetrachlorobenzene.

3. A process as claimed in Claim 1 or 2, wherein the alkali metal hydroxide is sodium hydroxide.

4. A process as claimed in Claim 1, 2 or 3, wherein the alcohol is methanol.

5. A process as claimed in any preceding Claim, wherein the reaction vessel pressure is maintained in the range of 250 to 700 p.s.i.g.

6. A process as claimed in any preceding claim, in which the alkali metal hydroxide in the mixture is added at a controlled rate in the range of 0.4 to 11 mol per hour.

7. A process as claimed in any preceding claim, in which sodium trichlorophenate is prepared by heating 1,2,4,5-tetrachlorobenzene in the closed reaction vessel to a temperature of 175° C., adding 11 mol per hour of sodium hydroxide contained in a mixture with methanol, the mol ratio of methanol to sodium hydroxide being 5.4:1, and maintaining the reaction temperature at 175° C. for a period of 3 hours, under a pressure of 270 to 490 p.s.i.g., the amount of methanol sodium hydroxide mixture being such as to provide a mol ratio of sodium hydroxide to tetrachlorobenzene of about 2.2:1.

8. A process of preparing an alkali metal polyhalophenate, as described with reference to the foregoing Examples.

9. Alkali metal polyhalophenates, when prepared by a process as claimed in any preceding claim.

POLLAK, MERCER & TENCH,
Chartered Patent Agents,
Audrey House, Ely Place, London, E.C.1.,
Agents for the Applicants.

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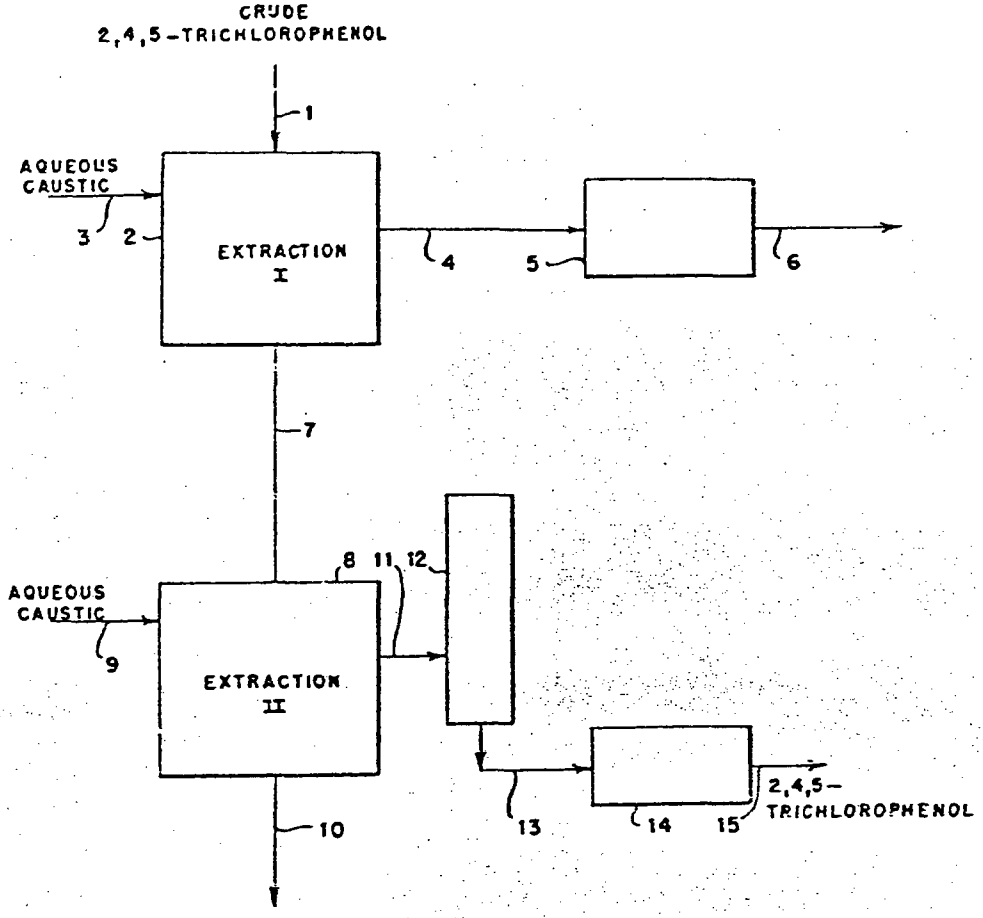
July 17, 1956 B. H. NICOLAISEN 2,755,307

PROCESS FOR THE RECOVERY OF 2,4,5-TRICHLOROPHENOL

Filed May 7, 1953



INVENTOR.
Bernard H. Nicolaisen
BY
Adams, Forward and McLean
ATTORNEYS

United States Patent Office

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Patented July 17, 1956

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PROCESS FOR THE RECOVERY OF 2,4,5-TRICHLOROPHENOL

Bernard H. Nicolaisen, Kenmore, N. Y., assignor to Olin Mathieson Chemical Corporation, a corporation of Virginia

Application May 7, 1953, Serial No. 353,659

1 Claim. (Cl. 260—623)

My invention relates to the production of 2,4,5-trichlorophenol by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene and in particular relates to the purification of the crude 2,4,5-trichlorophenol product so derived.

In the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene numerous contaminating products are formed. Methanol, for example, which may be used as a solvent for the hydrolysis reaction, tends to cause some production of trichloroanisole and dichlorodimethoxybenzene. The presence of the usual small amounts of other tetrachlorobenzene isomers, such as 1,2,3,4-tetrachlorobenzene, as impurities in the symmetrical 1,2,4,5-tetrachlorobenzene, causes the production of undesired position isomers of 2,4,5-trichlorophenol.

At the present time there exists a substantial demand for a high purity 2,4,5-trichlorophenol product which is not satisfied by the crude derived by the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene. The demand is, in particular, for a product having a melting point over 65° C. which in the molten state has a water-white color. The product must also be completely soluble in caustic solution, e. g. 0.1 N NaOH, and should be at least 99% pure.

Caustic-insoluble materials, such as trichloroanisole and dichlorodimethoxybenzene, may be removed to some extent by steam distillation of the alkaline phenate solution but complete removal of these impurities requires excessive amounts of steam. Other impurities, such as the position isomers of 2,4,5-trichlorophenol are more difficult to separate because of their similar chemical and physical properties.

A high purity 2,4,5-trichlorophenol product meeting the above specifications can be recovered from the crude trichlorophenol obtained by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene. I have found, in particular, that crude 2,4,5-trichlorophenol resulting from the acidification of the alkaline hydrolysis mixture can be separated into pure 2,4,5-trichlorophenol free from undesirable contaminants by a step-wise extraction with aqueous caustic.

The process of my invention thus essentially requires extracting crude 2,4,5-trichlorophenol with aqueous caustic solution sufficient in amount to convert all of the 2,3,6-trichlorophenol and other extraneous phenols present and a minor proportion of the 2,4,5-trichlorophenol to the water-soluble corresponding phenates. The operation is carried out at a temperature at which the phenols are in the liquid state. Unneutralized phenols are then separated from the dilute aqueous phenate solution.

The unneutralized phenols, separated from the aqueous phenate phase, are further extracted by the addition of aqueous caustic solution in an amount sufficient to convert substantially less than the total of the phenols present to the corresponding phenates. The extraction is again carried out at a temperature at which the phenols are in the liquid state. The aqueous phenate extract solution is then separated from the remaining undissolved oils. Acidification of this second extract yields the desired purified 2,4,5-trichlorophenol product which is separated and dried.

The remaining undissolved oils comprise trichlorophenols contaminated with alkali-insoluble impurities and are useful as crude trichlorophenol for most purposes not requiring the pure isomer. The phenate solution obtained in the first extraction step, although relatively impure, is also suitable for use after acidification as crude trichlorophenol. Alternatively, both fractions may be worked up for specific trichlorophenols or phenol ethers contained therein or they may be discarded.

My invention will be further illustrated by reference to the accompanying drawing which is a diagrammatic flow plan of the process.

Crude 2,4,5-trichlorophenol, obtained by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene followed by acidification, is introduced by line 1 to a first extraction step 2. The crude 2,4,5-trichlorophenol is extracted with aqueous caustic introduced by line 3 in an amount sufficient to convert all of the 2,3,6-trichlorophenol and a minor proportion of the 2,4,5-trichlorophenol to the water-soluble corresponding phenates.

Extract phenate solution is separated and removed by line 4. If desired, the phenates are acidified by means of a mineral acid in zone 5 and the phenols containing substantially all the 2,4,6-trichlorophenol and a few per cent of the 2,4,5-trichlorophenol of the original charge are removed by line 6.

The undissolved phenol residue from the aqueous phenate solution of extraction step 1 is separated and removed by line 7 to the second extraction step 8 and treated with aqueous caustic solution introduced by line 9 in an amount sufficient to convert less than the total quantity of the phenols contained in the residue to the corresponding phenates. The undissolved phenol residue after caustic treatment is removed by line 10.

The phenate extract solution is separated and removed by line 11. If desired, the phenate extract is steam distilled in zone 12 to improve the color of the 2,4,5-trichlorophenol. Steam distilled phenate extract is removed by line 13 and acidified by means of a mineral acid in zone 14 and 2,4,5-trichlorophenol is removed by line 15.

It is advantageous to use an aqueous caustic solution extracting agent containing not more than about 10% by weight of caustic since the employment of more concentrated caustic solutions results in dissolving a significant proportion of unneutralized phenols by the resulting aqueous phenate solution. Water should be added, therefore, to the aqueous extracting solution prior to or during each extraction, if required, to adjust the phenate concentration to not more than about 15% by weight to insure the separation of the unneutralized phenols as a separate phase which may be removed from contact with the aqueous phase.

The caustic used in the extraction process will ordinarily be sodium hydroxide but other alkali metal hydroxides, particularly potassium hydroxide, may also be used. The amount of caustic employed in the first extraction step preferably is sufficient to dissolve all of the 2,3,6-trichlorophenol and other extraneous phenols present and at least about 1 or 2% of the 2,4,5-trichlorophenol. The proportion of caustic used in the first extraction is thus dependent on the purity of the original crude 2,4,5-trichlorophenol. This in turn depends on the purity of the 1,2,4,5-tetrachlorobenzene employed to produce the crude 2,4,5-trichlorophenol. Less pure 2,4,5-trichlorophenol requires a greater amount of caustic in the first extraction step than when the crude trichlorophenol contains a smaller proportion of impurities. With very impure mixtures, the caustic may amount to sufficient to extract as much as one-third to one-half of the phenols present. The amount of caustic used to extract the residue from the first extraction step will range from about 25% to

about 95% of that required to extract the phenols present as water-soluble phenates.

Steam distillation before acidification of the crude 2,4,5-trichlorophenate solution resulting from the hydrolysis is extremely beneficial in that it removes some of the caustic insoluble impurities which otherwise are concentrated in the residual materials, making phase separation after each extraction progressively more difficult. Steam distillation thus reduces the proportion of remaining crude trichlorophenol to be reworked or discarded and further permits taking a larger heart cut of the crude product by caustic extraction in the second step and the recovery of a larger proportion of 2,4,5-trichlorophenol of the desired degree of purity. Steam distillation of the 2,4,5-trichlorophenol obtained by acidification of the second extraction is also advantageous in improving the color of the purified product.

While the extraction process of my invention is carried out at temperatures at which the trichlorophenol is liquid, the acidification of the extracts and recovery of phenols therefrom may be carried out at the same or lower temperatures. By acidifying the extracts at relatively low temperatures, the phenols may be precipitated as solids and removed by filtration. Alternatively, at elevated temperatures the trichlorophenol products may be obtained as liquids. The purity of the crude trichlorophenol and of the final products determines the limiting temperatures below which acidification of the extracts must be carried out in order to obtain the products as solids. However, all the operations are preferably carried out between about 20° and 80° C.

Example

A crude 2,4,5-trichlorophenol product (M. P. 60° to 62° C.) is obtained by acidifying the crude alkaline solution resulting from the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene and contains about 97% of 2,4,5-trichlorophenol, 1% of 2,3,6-trichlorophenol and about 2% of trichloroanisole and other impurities. The crude phenol is then extracted at about 70° C. with an amount of 5% aqueous sodium hydroxide calculated to convert about 5% of the phenols present to the corresponding sodium phenates. The extract solution after separation from undissolved phenols yields an impure product containing upon acidification substantially all of the 2,3,6-trichlorophenol and a few per cent of the 2,4,5-trichlorophenol of the original charge.

The separated trichlorophenol residue from the first extraction is then treated at about 70° C. with an amount of 5% aqueous sodium hydroxide calculated to convert about 90% of the original charge, calculated as 2,4,5-trichlorophenol to sodium 2,4,5-trichlorophenate.

After agitating and separating at about 70° C., the undissolved portion is removed and is combined with the crude trichlorophenols obtained by acidifying the first extract. Steam distilling the second extract solution before acidification aids materially in removing undissolved materials and results in an improvement in color of the 2,4,5-trichlorophenol obtained by subsequent acidification of the extract. The second extract solution, with or without the steaming operation, is then acidified by the use of mineral acid, for example sulfuric or hydrochloric acid, at 60° C. The liquid 2,4,5-trichlorophenol formed is separated from the aqueous salt solution, steam distilled, dried, and crystallized. The crystallized product has a melting point in excess of 65° C., is water-white in color, and is in excess of 99% purity.

I claim:

A process for the recovery of 2,4,5-trichlorophenol from crude mixtures thereof obtained by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene, which comprises extracting the crude 2,4,5-trichlorophenol at a temperature at which the mixture is in the liquid state with aqueous caustic solution in an amount calculated to convert the contaminating chlorophenols and a minor proportion of the 2,4,5-trichlorophenol present to the corresponding phenates, the resulting solution having a phenate concentration of not more than about 15 per cent by weight, separating the undissolved residue from the resulting aqueous phenate solution, extracting the separated residue at temperature at which the residue is liquid with aqueous caustic solution in an amount calculated to convert less than the total quantity of the phenols contained in the residue to the corresponding phenates, separating the resulting phenate extract solution from the remaining undissolved residue, and acidifying the extract solution to recover 2,4,5-trichlorophenol.

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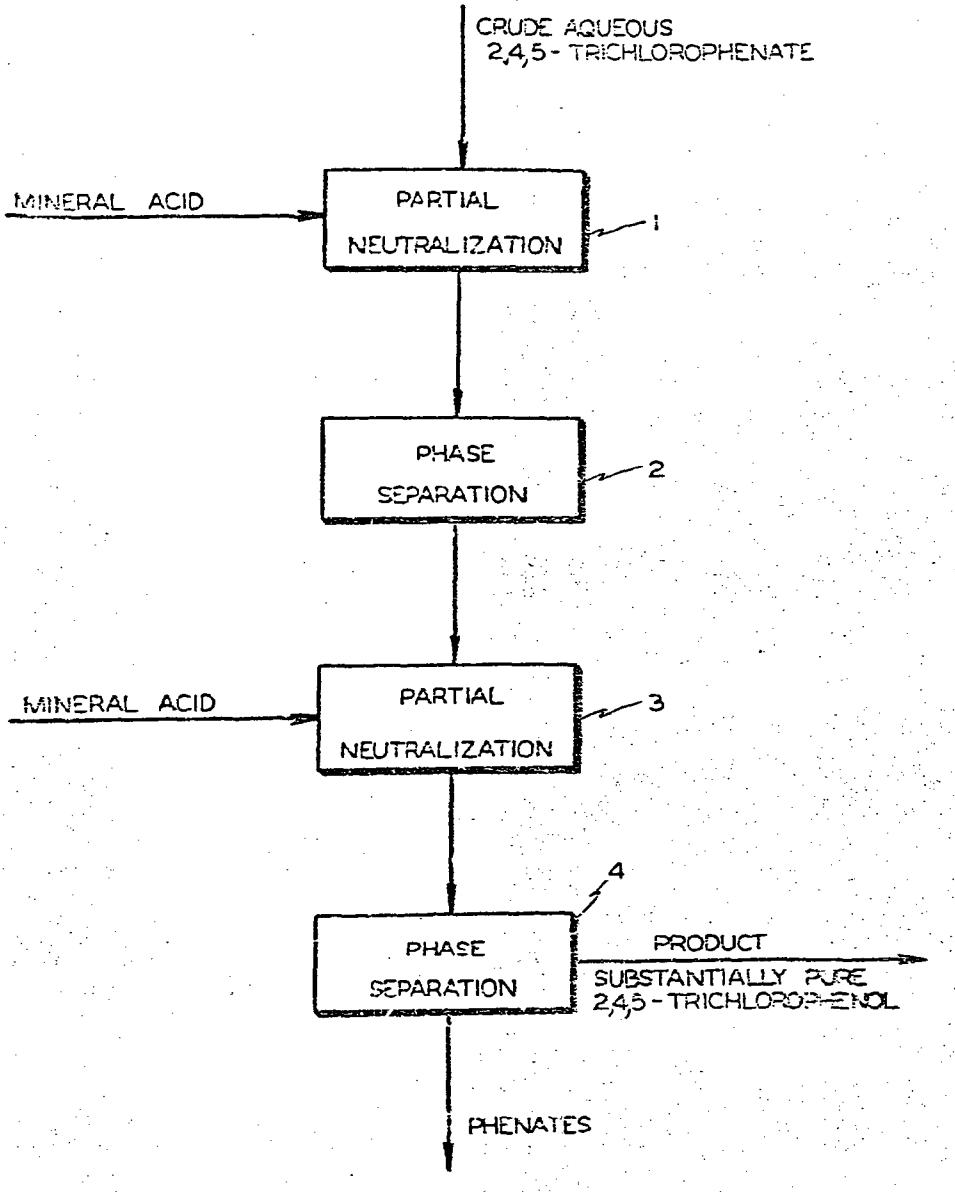
PROCESS FOR THE RECOVERY OF PURE 2,4,5-TRICHLOROPHENOL FROM PRODUCTS OF THE ALKALINE HYDROLYSIS OF 1,2,4,5-TETRACHLOROBENZENE

Filed Feb. 2, 1953



INVENTOR
THEODORE M. JENNEY
BERNARD H. NICOLAISEN

BY Adams Forward & McEwan
ATTORNEY

United States Patent Office

Patented May 22, 1956

2,748,174

PROCESS FOR THE RECOVERY OF PURE 2,4,5-TRICHLOROPHENOL FROM PRODUCTS OF THE ALKALINE HYDROLYSIS OF 1,2,4,5-TETRACHLOROBENZENE

Theodore M. Jenney and Bernard H. Nicolaisen, Kenmore, N. Y., assignors to Olin Mathieson Chemical Corporation, a corporation of Virginia

Application February 2, 1953, Serial No. 334,746

2 Claims. (Cl. 260—623)

Our invention relates to the production of 2,4,5-trichlorophenol by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene and in particular relates to the purification of the crude 2,4,5-trichlorophenol product so derived.

In the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene numerous contaminating products are formed. Methanol, for example, which may be used as a solvent for the hydrolysis reaction, tends to cause some production of trichloroanisole and dichlorodimethoxybenzene. The presence of the usual small amounts of other tetrachlorobenzene isomers, such as 1,2,3,4-tetrachlorobenzene, as impurities in the symmetrical 1,2,4,5-tetrachlorobenzene, causes the production of undesired position isomers of 2,4,5-trichlorophenol.

At the present time there exists a substantial demand for a high purity 2,4,5-trichlorophenol product which is not satisfied by the crude derived by the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene. The demand is, in particular, for a product having a melting point over 65° C. which in the molten state has a color from white to near white. The product must also be completely soluble in caustic solution, e. g. 0.1 N NaOH, and should be at least 99% pure.

Caustic insolubles, such as trichloroanisole and dichlorodimethoxybenzene, may be removed to some extent by steam distillation although their complete removal requires inordinately large amounts of steam. Other impurities, however, such as the position isomers of 2,4,5-trichlorophenol, are more difficult to separate because of their similar chemical and physical properties.

We have discovered that a high purity 2,4,5-trichlorophenol product meeting the above specifications may be recovered from the crude product obtained by the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene. We have found in particular that the solution of crude sodium 2,4,5-trichlorophenate which is recovered from the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene may be separated from the undesirable contaminants noted above by a step-wise neutralization process.

The process of our invention thus essentially requires neutralizing crude 2,4,5-trichlorophenate solution by addition of mineral acid thereto in an amount sufficient to neutralize excess alkalinity of the solution and a minor proportion of the phenates present. The neutralized phenates are released as the free phenols which separate from the dilute aqueous mixture as a separate phase, i. e. when the total phenate-phenol concentration is not more than about 10% by weight. Thus, we contemplate the addition of water, when required, to adjust the phenate-phenol concentration to not more than 10% by weight, either prior to the first neutralization step or immediately thereafter, whereby the resulting phenols are phased out and then may be separated from the aqueous phase which contains the remaining unneutralized phenates.

The aqueous phenate phase separated from the phenol phase is further neutralized by the addition of mineral acid but in an amount sufficient only for recovery as the free phenols of substantially less than the total of the phenates remaining in solution. The phenols phase out upon the second neutralization step without further adjustment of phenate concentration, and are separated from the aqueous phenate phase and recovered as the desired pure 2,4,5-trichlorophenol product.

The invention will be further described in conjunction with the accompanying drawing which comprises a flow sheet illustrating the essential features of the applicants' process.

In the drawing an aqueous solution of crude 2,4,5-trichlorophenate obtained by the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene is introduced to zone 1 of the flow sheet where it is contacted and partially neutralized with mineral acid. The phenols produced by the partial neutralization are separated in zone 2 by a phase separation based upon the insolubility of phenols in aqueous solutions having a phenol-phenate concentration of not more than about 10% by weight. The aqueous phenate solution is then subjected to a second partial neutralization in zone 3 by an additional quantity of mineral acid. The aqueous phenol-phenate solution is then subjected to a second phase separation of phenol in zone 4. The aqueous layer from this separation contains residual phenate which can be recovered as crude phenol and recycled. The phenol layer from the separation of zone 4 is the product, substantially pure 2,4,5-trichlorophenol.

The phenols precipitated in the first neutralization step, although they may be relatively impure, are suitable for use as crude trichlorophenol. The phenates remaining in solution after the second neutralization step may be recovered as the free phenols by complete neutralization and are also useful as crude trichlorophenol.

The amount of acid employed in the first neutralization steps ranges from an amount sufficient to neutralize the excess alkalinity and to spring free as little as about 1 or 2% of the phenates present up to an amount sufficient to spring free as much as a third or a half of the phenates present. The amount of acid added to neutralize the aqueous phase separated from the first neutralization step may range from about 25% to about 90 or 95% of that required to spring the phenates present as the corresponding phenols. The particular choice of proportion of acid added is largely dependent upon the purity of the original crude 2,4,5-trichlorophenate solution. In turn, the purity of this solution depends largely upon the purity of the 1,2,4,5-tetrachlorobenzene employed to produce the crude 2,4,5-trichlorophenate solution. More impure 2,4,5-trichlorophenate solutions require a greater amount of acid in the first neutralization step and a lesser amount in the second neutralization step. Generally, any mineral acid, such as sulfuric or hydrochloric acid, is suitable.

We have found that a pretreatment of the 2,4,5-trichlorophenate solution, such as by steam distillation to remove some of the caustic insoluble impurities, is extremely beneficial in that it lowers the required amount of acid for the first step of neutralization and permits a greater amount of acid to be employed in the second neutralization step, thus permitting highly increased yields of the recovered high purity products. Steam distillation of the product of the second neutralization is also advantageous as the color of the pure 2,4,5-trichlorophenol product is thus improved.

Our process is conveniently carried out at any temperature at which the phenate solution is in the liquid state, preferably between about 20° and about 80° C. The most important aspect of temperature is whether the phenols are to be phased out as solids or liquids; for the temperature at which the process is carried out must of course be selected having in mind whether a liquid-solid or a liquid-liquid separation is contemplated.

Example I

Crude 2,4,5-trichlorophenol obtained by acidifying the crude phenate product of the caustic hydrolysis of 1,2,4,5-tetrachlorobenzene and having the following analysis:

M. P., °C.	60–62
H_2O, wt. percent	0.00
Ash, wt. percent	0.05
Neutral equivalent	207
	(Theoretical 198.5)
2,4,5-trichlorophenol, wt. percent	97.0 (infra-red)
2,3,6-trichlorophenol, wt. percent	1.0 (infra-red)
2,4,5-trichloroanisole, wt. percent	1.0 (infra-red)
Unidentified (not tars), wt. percent	1.0 (approx.)

was reacted with caustic to a pH of 10 and steam distilled to remove trichloroanisole and some unidentified material, later proven to be dichlorodimethoxybenzene, from the phenate solution. To the resulting aqueous phenate solution was added one-third the amount of aqueous hydrochloric acid required to neutralize the slight excess of alkali and all the phenates present. Sufficient water was added to cause phase separation of the free phenols from the aqueous phenate solution, which was then decanted. The phenol layer was washed free of phenates with water and the washings added to the aqueous phenate layer. After steam distillation to separate color bodies the separated phenol contained 99% 2,4,5-trichlorophenol by infra-red analysis, was completely soluble in 0.1 NaOH solution, melted at 64–65° C. and had a neutral equivalent of 205–7.

An equal amount of hydrochloric acid was added to the residual phenate solution. The free phenol which was separated therefrom contained 100% 2,4,5-trichlorophenol by infra-red analysis, was completely soluble in 0.1 NaOH solution, melted at 65–65.5° C., had a neutral equivalent of 201, and was water white in the molten state.

A third cut was obtained by completely neutralizing the remaining phenates, resulting in precipitation of phenols which analyzed 98% 2,4,5-trichlorophenol and 1.5% 2,3,6-trichlorophenol by infra-red analysis.

Example II

In this example crude phenate solution, prepared as in Example I, was acidified step-wise following the procedure of Example I employing first 10% of the acid theoretically required to neutralize the slight excess alkalinity and all the phenates present as the free phenols, then 80% and then 10%. The steam distillation step was omitted and sufficient water was added before the first acidification to lower the phenate concentration to about 10% by weight. The first cut of phenols recovered was high in alkali insoluble organics containing only 67% 2,4,5-trichlorophenol by infra-red analysis. The center cut was 99.5% 2,4,5- and 0.5% 2,3,6-trichlorophenol by infra-red analysis and melted at 65.5–66° C. The third cut analyzed 98% 2,4,5-trichlorophenol.

In the following two examples all parts are by weight, unless otherwise noted.

Example III

100 parts of crude 2,4,5-trichlorophenol, having the same analysis as in Example I, are reacted with 20 parts sodium hydroxide in 950 parts water and 55 parts of washings from a previous batch to produce about 10% by weight phenate solution. 10% of the phenates are then phased out by addition of 10% of HCl (37% conc.) stoichiometrically required for complete neutralization. The phenols are separated by filtration and washed with 50 parts water, recovering 55 parts washings which are included in the preparation of the 10% phenate solution for a subsequent batch. The impure 2,4,5-trichlorophenol recovered from the washing operation is suitable for sale as crude trichlorophenol.

The filtrate of aqueous phenate solution is then treated with HCl (37% conc.) to phase out 80% of the phenates originally present as free phenols. The phenols are separated from the remaining aqueous layer by filtration and are washed with 50 parts water, recovering 60 parts washing which are added to the aqueous filtrate. The washed phenols are steam distilled and then dried to yield substantially pure 2,4,5-trichlorophenol.

The remaining filtrate, including 60 parts washings, noted above, is then treated with HCl (37% conc.) to spring free the remaining phenates as the phenols. The phenols which phase out are separated by filtration and are recovered for sale as crude trichlorophenols. About half the last group of phenols do not phase out and remain dissolved in the filtrate of the third neutralization step. They also may be recovered for crude sales.

Example IV

250 parts of crude 2,4,5-trichlorophenol of the same analysis as that employed in Example I are reacted with 50 parts sodium hydroxide in 250 parts water. 24.8 parts HCl (37% conc.) are added to spring free a portion of the phenates as the phenols. 2000 parts water are then added to phase out the phenols which are separated from the aqueous phenate phase by filtration. The phenols are washed and 16 parts recovered as crude trichlorophenol. The washings, combined with the aqueous filtrate, are treated with 100 parts HCl (37% conc.) to phase out 212.9 parts of 2,4,5-trichlorophenol which is washed and steam distilled to recover 165.6 parts pure 2,4,5-trichlorophenol. The washings, combined with the aqueous filtrate, are further treated with 27.2 parts HCl (37% conc.) to recover 3.2 parts of crude trichlorophenol.

We claim:

1. A process for the production of 2,4,5-trichlorophenol from aqueous mixtures of crude 2,4,5-trichlorophenate obtained by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene, which comprises adding mineral acid to the crude 2,4,5-trichlorophenate mixture in amount sufficient to neutralize excess alkalinity and a minor proportion of the phenates present, which form corresponding phenols, separating the phenols as separate phase from dilute aqueous mixture having a phenol-phenate content of not more than about 10% by weight, adding mineral acid to the separated aqueous phase in an amount sufficient to convert less than the total quantity of remaining phenates to corresponding phenols, and separating 2,4,5-trichlorophenol from the aqueous phase.

2. A process for the recovery of 2,4,5-trichlorophenol from crude mixtures thereof obtained by caustic hydrolysis of 1,2,4,5-tetrachlorobenzene, which comprises adding aqueous caustic solution to crude 2,4,5-trichlorophenol to convert all phenols present to the corresponding phenates, adding mineral acid to the crude 2,4,5-trichlorophenate mixture in amount sufficient to neutralize excess alkalinity and a minor proportion of the phenates present, which form corresponding phenols, separating the phenols as a separate phase from dilute aqueous mixture having a phenol-phenate content of not more than about 10% by weight, adding mineral acid to the separated aqueous phase in an amount sufficient to convert less than the total quantity of remaining phenates to the corresponding phenols, and separating 2,4,5-trichlorophenol from the aqueous phase.

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PREPARATION OF 2,4,5-TRICHLOROPHENOL

Edward Joseph Nikawitz, Passaic, and William S. Gump, Upper Montclair, N. J., assignors to The Givaudan Corporation, a corporation of New Jersey

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5 Claims. (Cl. 260—623)

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This invention relates to a process for preparing 2,4,5-trichloro phenol, and more especially to a process wherein 1,2,4,5-tetrachloro benzene is subjected to alkaline hydrolysis in the presence of ethylene- or propylene glycol (propanediol-1,2).

2,4,5-trichloro phenol has been prepared from 1,2,4,5-tetrachloro benzene by hydrolyzing the latter with alkali in the presence of methyl alcohol, the process being conducted under considerable pressure, of the order of 600–800 pounds per square inch. Special pressure equipment is required for conducting such a process. Moreover, appreciable amounts of the methyl ether of 2,4,5-trichloro phenol form when methyl alcohol is employed; and the formation of the ether is undesirable as it decreases the yield of the desired free phenol.

Our present invention overcomes the foregoing disadvantages and provides a process for making 2,4,5-trichloro phenol from 1,2,4,5-tetrachloro benzene which can be conducted with cheaper and simpler equipment than is required by the prior art process, and which does not result in the formation of any appreciable amount of ether.

In general, our process may be conducted by dissolving an alkali metal hydroxide, such as sodium hydroxide, potassium hydroxide and lithium hydroxide, in ethylene glycol or propylene glycol, or a mixture thereof, at elevated temperatures while stirring the contents. The tetrachloro benzene is then added and the mixture is heated for a few hours, normally 3–4 hours being sufficient. The end point of the reaction can be determined easily by taking a sample of the reaction mixture and diluting it with water. If the sample is water soluble or practically entirely soluble in the water, the reaction may be considered to have been completed. The desired phenol may be isolated in accordance with known procedures. For example, the reaction mixture may be cooled after the test as above shows substantial completion of the reaction, and then acidified with a mineral acid such as hydrochloric acid. The precipitated alkali metal chloride is filtered off. The filtrate is poured into water, causing the 2,4,5-trichloro phenol to precipitate. The phenol is extracted with benzene and the benzene extract is distilled to remove the benzene and yield the phenol. The aqueous layer remaining after the benzene extraction is fractionally distilled to remove the glycol employed.

The proportions of the ingredients used may

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be varied. The alkali metal hydroxide is used in amounts equivalent to at least 2 mols of hydroxide per mol of tetrachloro benzene. 2–3 mols of hydroxide per mol of tetrachloro benzene gives excellent results. Higher amounts of hydroxide may be employed, but are unnecessary.

With regard to the amount of glycol which should be employed in our process, we find that excellent results are obtained when about 750 grams of the glycol per 216 grams (1 mol) of the tetrachloro benzene are used. Larger amounts of glycol may be used, but in such cases no advantageous results follow. Amounts less than 450 grams of glycol per 216 grams of tetrachloro benzene are not recommended, as yield and quality of the desired phenol are adversely affected.

The temperature range at which the hydrolysis may be effected is between about 160° C. and 200° C., the preferred range being between about 170° C. and 180° C. Higher temperatures are obtainable when propylene glycol is employed than is the case when ethylene glycol is employed.

A special advantage of this process is that it can be conducted at atmospheric pressure, under reflux. However, if desired, the contents may be heated in a closed system, whereby a slight pressure is built up, amounting however to not more than 15 to 20 pounds per square inch, and not necessitating the use of any special pressure equipment in the plant.

The invention is illustrated by the following examples without however limiting the same to them.

Example I

60 grams of sodium hydroxide flakes (95% NaOH) were dissolved in 500 grams of ethylene glycol in a 2 liter three-necked flask provided with stirrer and an air condenser. The contents were heated to 150° C.–160° C., this step requiring about 30 minutes. 144 grams of 1,2,4,5-tetrachloro benzene were rapidly added to the solution, and the mixture was heated to 170° C.–180° C. (inside temperature), and maintained at that temperature range for 4 hours. 10 grams of tetrachloro benzene sublimed in the air condenser and were recovered. A sample of the reaction mixture gave a clear solution when dissolved in 10 times its weight of water.

The reaction mixture was allowed to cool; dry hydrogen chloride was passed into it until it became acid to litmus. The slight excess of hydrogen chloride was neutralized by the addition of a small amount of sodium bicarbonate. After cooling again to about 20° C., the salt was filtered

by suction and the salt cake was washed with 50 cc. of isopropyl alcohol. 500 cc. of water were added to the filtrate resulting in a bottom layer of precipitated trichloro phenol and a top layer of dilute ethylene glycol. The entire mixture was extracted with 400 cc. of benzene, then with 100 cc. of benzene and finally with 80 cc. of benzene.

The combined benzene extracts were shaken with 200 cc. of water and the water layer was separated and added to the dilute ethylene glycol. The washed combined benzene extracts were dried by means of anhydrous sodium sulfate, filtered, and distilled. After removal of the benzene, the residue was distilled at a pressure of 4 mm. of mercury. 106 grams of 2,4,5-trichloro phenol, boiling at 101° C.–105° C., and having a congealing point of 63.3° C. (uncorrected), were obtained.

The ethylene glycol can be recovered by distillation of the aforementioned dilute ethylene glycol. The water and isopropyl alcohol were removed in a fractionating still at a pressure of 90 mm. of mercury, the temperature being carried up to 50° C. The ethylene glycol was then distilled under high vacuum (3 mm.), 232 grams of the glycol boiling at 80° C. being recovered. In order to remove practically all of the ethylene glycol from the small amount of salt remaining in the distilling flask, the temperature was raised so that some glycol, boiling from 80° C. to 120° C., was obtained.

Example II

72 grams of 1,2,4,5-tetrachloro benzene were stirred and heated to 190–200° C. with a solution of 30 grams of sodium hydroxide in 250 grams of propylene glycol, the heat treatment being conducted for 6 hours. 24 grams of concentrated sulfuric acid (93% H_2SO_4) were added to the reaction contents after they were cooled to room temperature (about 25° C.). The entire contents were poured into 1000 cc. of water. The solid material was then filtered and washed with 500 cc. of water and finally dissolved in 200 cc. of benzene. The benzene solution was dried with anhydrous sodium sulfate and then filtered.

After removal of the benzene by distillation, the residue was distilled under a high vacuum (5 mm.), 45 grams of 2,4,5-trichloro phenol being obtained thereby.

The foregoing illustrates the practice of this invention, which however, is not to be limited thereby but is to be construed as broadly as permissible in view of the prior art and limited solely by the appended claims.

We claim:

1. The process for preparing 2,4,5-trichlorophenol, which comprises heating at 160°–200° C. in the following proportions: 1 gram molecular weight of 1,2,4,5-tetrachloro benzene and at least 2 gram molecular weights of an alkali metal hydroxide in the presence of at least 450 grams of at least one material from the group consisting of ethylene glycol and propylene glycol, the reaction being conducted under a pressure within the range of that of the atmosphere up to 20 pounds per square inch and for a time sufficient to substantially complete the conversion into 2,4,5-trichlorophenol.

2. The process for preparing 2,4,5-trichlorophenol, which comprises heating at 160°–200° C. in the following proportions: 1 gram molecular weight of 1,2,4,5-tetrachloro benzene and at least 2 gram molecular weights of an alkali metal hydroxide in the presence of at least 450 grams of ethylene glycol, the reaction being conducted under a pressure within the range of that of the atmosphere up to 20 pounds per square inch and for a time sufficient to substantially complete the conversion into 2,4,5-trichlorophenol.

3. The process for preparing 2,4,5-trichlorophenol, which comprises heating at 160°–200° C. in the following proportions: 1 gram molecular weight of 1,2,4,5-tetrachloro benzene and at least 2 gram molecular weights of sodium hydroxide in the presence of at least 450 grams of ethylene glycol, the reaction being conducted under a pressure within the range of that of the atmosphere up to 20 pounds per square inch and for a time sufficient to substantially complete the conversion into 2,4,5-trichlorophenol.

4. The process for preparing 2,4,5-trichlorophenol, which comprises heating at 170°–180° C. in the following proportions: 1 gram molecular weight of 1,2,4,5-tetrachloro benzene and 2–3 gram molecular weights of sodium hydroxide in the presence of 750 grams of ethylene glycol, the reaction being conducted under atmospheric pressure and for a time sufficient to substantially complete the conversion into 2,4,5-trichlorophenol.

5. The process for preparing 2,4,5-trichlorophenol, which comprises heating at 170°–180° C. in the following proportions: 1 gram molecular weight of 1,2,4,5-tetrachloro benzene and 2–3 gram molecular weights of sodium hydroxide in the presence of 750 grams of propylene glycol, the reaction being conducted under atmospheric pressure and for a time sufficient to substantially complete the conversion into 2,4,5-trichlorophenol.

EDWARD JOSEPH NIKAWITZ.
WILLIAM S. GUMP.

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Virgilio et al.

[11] 4,216,342
[45] Aug. 5, 1980

[54] PROCESS FOR THE PURIFICATION OF CRUDE 2,4,5-TRICHLOROPHENOL

[75] Inventors: Joseph A. Virgilio, Wayne; Joachim E. Freudewald, Morristown, both of N.J.

[73] Assignee: Givaudan Corporation, Clifton, N.J.

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[52] U.S. Cl. 568/755; 568/776
[58] Field of Search 568/755, 725, 776, 727

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Primary Examiner—Werren B. Lone
Attorney, Agent, or Firm—Robert F. Tavares; Thomas Cifelli, Jr.

[57] ABSTRACT

A novel process for the purification of 2,4,5-trichlorophenol which comprises selectively reacting the major impurities with formaldehyde.

11 Claims, No Drawings

PROCESS FOR THE PURIFICATION OF CRUDE 2,4,5-TRICHLOROPHENOL

BACKGROUND OF THE INVENTION

The conventional industrial method for preparing 2,4,5-trichlorophenol involves the reaction of 1,2,4,5-tetrachlorobenzene with methyl alcoholic or aqueous methyl alcoholic sodium hydroxide. The crude product which is available commercially is about 94% 2,4,5-trichlorophenol and about six percent impurities which are primarily dichlorophenols and dichloromethoxyphenols.

The germacide known as Hexachlorophene® (bis-[3,5,6-trichloro-2-hydroxyphenyl]methane), is prepared by condensing 2,4,5-trichlorophenol with formaldehyde. In order to get a germicide of high purity, it is desirable to start with a 2,4,5-trichlorophenol of high purity. Since the dichlorophenols and dichloromethoxyphenols present in the commercial grade 2,4,5-trichlorophenol will also react with formaldehyde, it is desirable to remove them prior to the condensation.

SUMMARY OF THE INVENTION

It is the surprising and unexpected finding of this invention that major impurities in the crude product (ca. 94% 2,4,5-trichlorophenol and ca. 5.5% dichlorophenols + dichloromethoxyphenols) can be reacted with formaldehyde under conditions wherein the undesired 5.5% of the impurities react to form condensation products, but the 2,4,5-trichlorophenol does not react to form Hexachlorophene. The unreacted 2,4,5-trichlorophenol can then be separated from the condensation products to provide 99.5% pure 2,4,5-trichlorophenol in high yield.

The critical parameters in this process appear to be the concentration of sulfuric acid, the reaction temperature and the time the reaction is allowed to run.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method disclosed herein depends upon the ability to judiciously choose reaction conditions wherein the undesirable impurities will form condensation products with the formaldehyde while the 2,4,5-trichlorophenol will not.

The form of the formaldehyde is not critical. Formaldehyde added as a 37% aqueous solution or formaldehyde added as paraformaldehyde are both suitable.

The nature or amount of excess of the formaldehyde used does not appear to be critical. Although stoichiometry demands only one mole of formaldehyde for every two moles of phenolic impurity to be condensed, it is preferred to add an excess of several fold since the reagent is economical and an excess does not have a detrimental effect on the purification process.

An amount of formaldehyde greater than 1 mole per mole of impurity to be removed would be suitable with an amount of 2 to 5 moles/mole preferred. About 3 moles per mole is especially preferred.

The concentration of the sulfuric acid appears to be the most critical factor. When the sulfuric acid concentration is 50% or less, the yields of recovered 2,4,5-trichlorophenol were lower and the improvement in the purity was only marginal. When the concentration of sulfuric acid is 80% or greater, the 2,4,5-trichlorophenol reacts rapidly with the formaldehyde and the result is a lower recovery of 2,4,5-trichlorophenol and

only a marginal, if any, improvement as to the purity of the recovered material.

By contrast, at sulfuric acid concentrations between 55% and 75% there is a surprising selectivity demonstrated with the formaldehyde reaction primarily with the dichlorophenol and methoxydichlorophenol impurities and not with the 2,4,5-trichlorophenol. It is preferred to work at the center of this range of concentrations, i.e. at concentrations of 60% to 70%.

The temperature range is less critical than the acid concentration, but should be carefully controlled to insure maximum recovery of high quality 2,4,5-trichlorophenol. Temperatures below 70° C. result in a sluggish reaction between the impurities to be removed and the formaldehyde resulting in a poorer grade of recovered 2,4,5-trichlorophenol.

At temperatures exceeding 90° C. the reaction appears to be less selective and lower yields of recovered 2,4,5-trichlorophenol are obtained. Temperatures in the range of 70° C. to 90° C. are, therefore, preferred. It is especially preferred to work in the middle of this range at temperatures of from 75° C. to 85° C.

The reaction should, of course, be run until all of the impurities to be removed have condensed with the formaldehyde. Under the preferred conditions, this normally occurs from five to eight hours. It is preferred however, to follow the reaction by a suitable analytical tool such as gas liquid chromatography.

The purified 2,4,5-trichlorophenol can be separated from the heavier condensation products by methods known in the art, i.e. by extraction and/or distillation.

A number of suitable extraction solvents will dissolve the trichlorophenol, but not the less soluble bis-phenols. Suitable for this purpose are the alkane solvents such as pentane, hexane, heptane and the like.

It is preferred to separate the lower boiling trichlorophenol from the higher boiling condensation products by a distillation, preferably a steam distillation or vacuum steam distillation.

ILLUSTRATION OF THE PREFERRED EMBODIMENTS

A number of examples are provided herein to illustrate the preferred embodiments of this invention. They are included for the purpose of illustration only and should not be construed as limiting. They are intended to embrace any equivalents or obvious extensions which are known or should be known to a person skilled in the art.

The purity of the 2,4,5-trichlorophenol was determined by vapor phase chromatography using a ¼ in. × 6 ft. stainless steel column packed with 4% FFAP on 100/120 mesh chromsorb W, acid washed, DMCS. A flame ionization detector was used.

The commercial technical grade 2,4,5-trichlorophenol that was purified in these examples was purchased from vendors who are in the business of manufacturing and selling this material and was analysed by gas liquid chromatography as follows:

2,4,5-Trichlorophenol	94.0 ± 0.2%
2,4/2,5-Dichlorophenol	1.0 ± 0.8%
2,3,6/2,4,6-Trichlorophenol	0.3 ± 0.3%
3,4-Dichlorophenol	0.1 ± 0.1%
4,5-Dichloro-2-methoxyphenol 2,5-Dichloro-4-methoxyphenol	4.6 ± 0.7%

-continued

2,4-Dichloro-5-methoxyphenol

The term technical grade TCP refers to a commercially available product similar to that described above and which is about 94% 2,4,5-trichlorophenol. This term (technical grade TCP) when used hereinafter refers to such a commercially available product.

EXAMPLE I

Sulfuric acid (903 grams of 93% H_2SO_4) was diluted by slowly adding it to cold water (347 g) which was cooled and stirred during the addition. Technical grade TCP was added and the reaction mixture heated to and subsequently maintained at 80° C.

Aqueous formaldehyde (14.0 g of a 37% solution) was added slowly over a period of four hours. The reaction mixture was maintained at 80° C. for an additional two hours.

The reaction mixture was diluted by adding about 600 ml water and the product isolated via a steam distillation.

There was obtained 206.5 g of 2,4,5-trichlorophenol which was 99.5% pure. This represents an 87.7% recovery of the 2,4,5-trichlorophenol in the starting material.

The purified product analysed as follows:

2,4,5-Trichlorophenol	99.5
2,4/2,5-Dichlorophenol	—
2,3,6/2,4,6-Trichlorophenol	0.3
3,4-Dichlorophenol	—
4,5-Dichloro-2-methoxyphenol 2,5-Dichloro-4-methoxyphenol 2,4-Dichloro-5-methoxyphenol	0.2

EXAMPLE II

Example I was repeated, substituting 5 g of paraformaldehyde for the 14 g of 37% aqueous formaldehyde. The paraformaldehyde was added portionwise over a 30 minute period.

Pure 2,4,5-trichlorophenol (200.9 g, 85.5% yield, 99.6% pure) was recovered.

EXAMPLE III

Example I was repeated excepting that 21 g of aqueous formaldehyde was used.

Pure 2,4,5-trichlorophenol (200.9 g, 85.5% yield, 99.7% pure) was recovered.

EXAMPLE IV

The process of Example II was repeated using a hot heptane extraction in place of the steam distillation.

There was 190.6 g of 2,4,5-trichlorophenol recovered (91.1% yield, 98.3% pure).

EXAMPLE V

Example I was repeated excepting that a temperature of 100° C. was used. There was 167.1 g of 2,4,5-trichlorophenol recovered (71.0% yield, 99.6% pure). This is considerably less than obtained in Example I illustrating the fact that temperatures in excess of 90° C. result in lower recovery of the desired product.

EXAMPLE VI

Example II was repeated excepting that a sulfuric acid concentration of 50% was used. Product recovered was only 96.2% pure. This illustrates the poor results obtained at low acid concentrations.

EXAMPLE VII

Example I was repeated and followed by gas liquid chromatography to illustrate the shorter reaction times result in a product of lower purity.

After 1 hr 94.7% pure 2,4,5-trichlorophenol recoverable.

After 2 hrs 95.1% pure 2,4,5-trichlorophenol recoverable.

After 4 hrs 98.7% pure 2,4,5-trichlorophenol recoverable.

After 6 hrs. 99.5% pure 2,4,5-trichlorophenol recoverable.

EXAMPLE VIII

Example I was repeated and the 2,4,5-trichlorophenol was recovered via a vacuum steam distillation.

There was recovered 208.0 g (88.5% yield, 99.3% pure).

EXAMPLE IX

Example I was repeated excepting that the concentration of the sulfuric acid used was 80%. The 2,4,5-trichlorophenol reacted with the formaldehyde to form a bis-phenol. This example illustrates the failure of the purification process if the concentration of acid gets too high.

We claim:

1. Process for the purification of technical grade TCP which comprises treating the technical grade TCP with formaldehyde in the presence of 55% to 75% sulfuric acid at a temperature between 70° C. and 90° C. and separating purified TCP therefrom.

2. A process according to claim 1 wherein the purified TCP is isolated by a distillation or an extraction.

3. A process according to claim 2 wherein the purified TCP is isolated by a steam distillation or a vacuum steam distillation.

4. A process according to claim 1 wherein 60–70% sulfuric acid is used.

5. A process according to claim 4 wherein the temperature is between 75° C. and 85° C.

6. A process according to claim 5 wherein the product is isolated by a distillation or an extraction.

7. A process according to claim 6 wherein the product is isolated by a distillation.

8. A process according to claim 1 wherein there is used:

(a) two to five molar equivalents of formaldehyde

(b) 60% to 70% sulfuric acid;

(c) a reaction temperature of 75° C. to 85° C.;

(d) a steam distillation or vacuum steam distillation for the isolation of the purified 2,4,5-trichlorophenol.

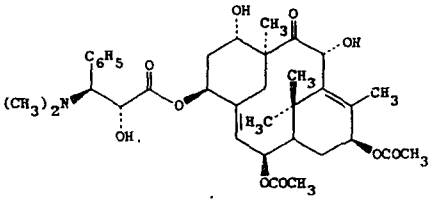
9. The process of claim 8 wherein the reaction time is 5 to 8 hours.

10. The process of claim 9 wherein aqueous formaldehyde is used.

11. The process of claim 9 wherein paraformaldehyde is used.

* * * * *

F. Manske, Ed. (Academic Press, New York, 1968) pp 597-626.

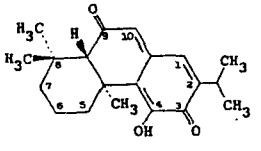


taxine A

Granular amorph powder, mp 121-124°. $[\alpha]_D^{17}$ +95.7° (c = 4.59 in ethanol). Sol in ether, chloroform, alcohol; practically insol in water, petr ether. Undoubtedly responsible for the poisonous properties of the yew. Fatalities among domestic animals due to yew poisoning are not uncommon today. Human fatal symptoms are those of gastrointestinal irritation, cardiac and respiratory failure.

Taxine A, $C_{35}H_{47}NO_{10}$, mp 204-206°. $[\alpha]_D$ −140° ($CHCl_3$).

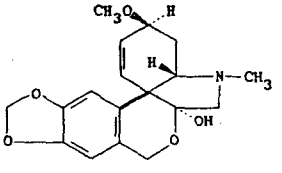
8955. Taxodione. *4b,5,6,7,8,8a-Hexahydro-4-hydroxy-4b,8,8-trimethyl-2-(1-methylethyl)-3,9-phenanthrenedione; 11-hydroxy-13-isopropylpodocarpa-7,9(11),13-triene-6,12-dione.* $C_{20}H_{26}O_3$; mol wt 314.43. C 76.40%, H 8.34%, O 15.26%. Isoln of naturally occurring (+)-form from *Taxodium distichum* Rich, *Taxodiaceae:* Kupchan *et al., J. Am. Chem. Soc.* **90,** 5923 (1968). Structure: *eidem, J. Org. Chem.* **34,** 3912 (1969). Total synthesis of the racemate: Mori, Matsui, *Tetrahedron* **26,** 3467 (1970); T. Matsumoto *et al., Bull. Chem. Soc. Japan* **44,** 2766 (1971); **50,** 1575 (1977); D. L. Snitman, R. J. Himmelsbach, *Tetrahedron Letters* **1979,** 2477; R. V. Stevens, G. S. Bisacchi, *J. Org. Chem.* **47,** 2396 (1982). Total synthesis of the (+)-form: T. Matsumoto *et al., Bull. Chem. Soc. Japan* **50,** 266 (1977). Antitumor activity studies: Hanson *et al., Science* **168,** 378 (1970).



Golden plates from methanol. mp 115-116°. $[\alpha]_D^{25}$ +56° (c = 1 in $CHCl_3$). uv max (methanol): 320, 332, 400 nm (ε 25,000, 26,000, 2000).

THERAP CAT: Antineoplastic.

8956. Tazettine. *Sekisanine; sekisanoline; ungernine.* $C_{18}H_{21}NO_5$; mol wt 331.26. C 65.24%, H 6.39%, N 4.23%, O 24.14%. From *Narcissus tazetta* L., *Lycoris radiata* Herb., *Ungernia sewerzowi* (Rgl.) Fedtsch., and other *Amaryllidaceae:* Späth, Kahovec, *Ber.* **67,** 1501 (1934). Structure and stereochemistry: Ikeda *et al., J. Chem. Soc.* **1956,** 4749. Abs config: Highet, Highet, *Tetrahedron Letters* **1966,** 4099. Synthesis: Hendrickson *et al., J. Am. Chem. Soc.* **92,** 5538 (1970); Tsuda *et al., Tetrahedron Letters* **1972,** 3153. Biosynthesis: Fales, Wildman, *J. Am. Chem. Soc.* **86,** 294 (1964). Identity with sekisanine and sekisanoline: Ikeda *et al., loc. cit.* Stereospecific total synthesis: Hendrickson *et al., J. Am. Chem. Soc.* **96,** 7781 (1974); S. Danishefsky *et al., ibid.* **102,** 2838 (1980); **104,** 7591 (1982).

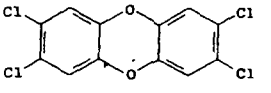


Crystals, mp 210-211° (evac tube); racemate reported as mp 237-238° (Tsuda) and mp 175-176° (Danishefsky). $[\alpha]_D^{25}$ +150.3° (82 mg in 2 ml chloroform). Sol in methanol, ethanol, choroform. Sparingly sol in ether.

Hydrochloride, crystals, mp 206°, water soluble.

Methiodide, crystals, dec 220° (evacuated tube).

8957. TCDD. *2,3,7,8-Tetrachlorodibenzo[b,e][1,4]dioxin; 2,3,7,8-tetrachlorodibenzo-p-dioxin;* 2,3,6,7-tetrachlorodibenzodioxin; dioxin; TCDBD. $C_{12}H_4Cl_4O_2$; mol wt 321.96. C 44.77%, H 1.25%, Cl 44.04%, O 9.94%. Highly toxic and teratogenic contaminant of 2,4,5-trichlorophenol and 2,4,5-T, *q.q.v.*, can be formed during the manufacture of trichlorophenol. Prepn by chlorination of dibenzo-*p*-dioxin: W. Sandermann, *Ber.* **90,** 690 (1957); M. Tomita *et al., Yakugaku Zasshi* **79,** 186 (1959), *C.A.* **53,** 13152d (1959); by condensation of potassium 2,4,5-trichlorophenate: O. Aniline in *Chlorodioxins—Origin and Fate,* E. H. Blair, Ed., *Advances in Chemistry Series* **120** (A.C.S., Washington, D.C., 1973) pp 126-135. Crystal structure: F. P. Boer *et al., Acta Crystallogr.* **28B,** 1023 (1972). Toxicity and metabolism studies: R. J. Kociba *et al., Toxicol. Appl. Pharmacol.* **35,** 553 (1976); J. Q. Rose *et al., ibid.* **36,** 209 (1976); A. Poland, A. Kende, *Fed. Proc.* **35,** 2404 (1976). Environmental degradation: D. G. Crosby, A. S. Wong, *Science* **195,** 1337 (1976). Review of carcinogenicity studies: *IARC Monographs* **15,** 41-102 (1977). Comprehensive reviews of formation, chemistry, and toxic and environmental effects: *Chlorodioxins—Origin and Fate,* E. H. Blair, Ed., *loc. cit.* 141 pp; *Environ. Health Perspect.* **5,** 313 pp (1973); R. D. Kimbrough, *Crit. Rev. Toxicol.* **2,** 445-498 (1974); A. Poland, J. C. Knutson, *Ann. Rev. Pharmacol. Toxicol.* **22,** 517-554 (1982). *See also: Dioxin—Toxicological and Chemical Aspects,* F. Cattabeni *et al.,* Eds. (Wiley, New York, 1978) 222 pp; special issue, *Chem. & Eng. News* **61** (June 6, 1983).



Needles, mp 295° (Tomita); crystals from anisole, mp 320-325° (Sandermann). LD_{50} orally in male, female rats (mg/kg): 0.022, 0.045, B. A. Schwetz *et al.* in *Chlorodioxin—Origin and Fate, loc. cit.* pp 55-69.

Note: An industrial accident during the manufacture of 2,4,5-trichlorophenol in Seveso, Italy on July 10, 1976 caused the release of an estimated two to ten pounds of TCDD into the environment. Concentrations as high as 51.3 ppm TCDD were found in some samples: R. Rawls, D. A. O'Sullivan, *Chem. & Eng. News* **54,** 27 (Aug. 23, 1976); A. Hay, *Nature* **262,** 636 (1976).

TCDD, as a contaminant created in the manufacture of *Agent Orange,* a widely used defoliant in Vietnam during the 1960's, has also been implicated as the causative agent of various symptoms described by veterans exposed to the defoliant, *see* C. Holden, *Science* **205,** 770 (1979).

Caution: Extremely potent, low molecular weight toxin. Toxic effects in animals include anorexia, severe weight loss, hepatotoxicity, hepatoporphyria, vascular lesions, chloracne, gastric ulcers, teratogenicity and delayed death. Industrial workers exposed to TCDD have developed chloracne, porphyrinuria and porphyria cutanea tarda. *See* Poland, Kende, *loc. cit.*, C. D. Carter *et al., Science* **188,** 738 (1975). This substance has been listed as a carcinogen by the EPA: *Second Annual Report on Carcinogens* (NTP 81-43, Dec. 1981) pp 226-227.

8958. Technetium. Tc; at. wt (longest-lived isotope) 98; at. no. 43. Usual valences 4 and 7. Trivalent Tc less common. Radioactive element. Discovery claimed by Noddack, Tacke, and Berg who called it "masurium"; the existence of masurium has never been confirmed by isoln of the element. Element no. 43 is the first artificially produced element. Named from the Greek word for "artificial"; separated from a molybdenum plate that had been bombarded for a few months with a strong beam of deuterons in the Berkeley cyclotron: Perrier, Segré, *Nature* **140,** 193 (1937); *eidem, J. Chem. Phys.* **5,** 712 (1937); Cacciapuoti, Segré, *Phys. Rev.* **52,** 1252 (1937). The most commonly available isotope, ^{99}Tc,

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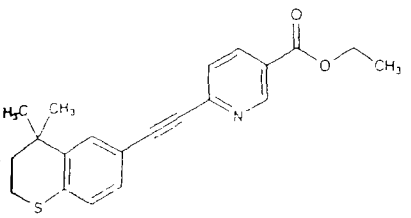
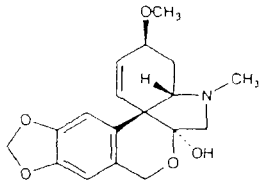


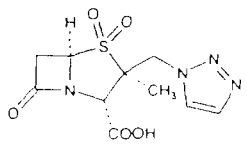
...ite solid
...AP CAT Antiacne; antipsoriatic.

...50. Tazettine. Sekisanine; sekisanoline; ungernine. ...NO_3; mol wt 331.37. C 65.24%, H 6.39%, N 4.23%, ...14%. From *Narcissus tazetta* L., *Lycoris radiata* Herb., ...*ia sewerzowi* (Rgl.) Fedtsch., and other *Amaryllida-* ...Späth, Kahovec, *Ber.* 67, 1501 (1934). Structure and ...chemistry: Ikeda *et al., J. Chem. Soc.* 1956, 4749. ...onfig: Highet, Highet, *Tetrahedron Letters* 1966, ...Synthesis: Hendrickson *et al., J. Am. Chem. Soc.* 92, ...(1970); Tsuda *et al., Tetrahedron Letters* 1972, 3153. ...nthesis: Fales, Wildman, *J. Am. Chem. Soc.* 86, 294 ...): Identity with sekisanine and sekisanoline: Ikeda *et ...c. cit.* Stereospecific total synthesis: Hendrickson *et ...Am. Chem. Soc.* 96, 7781 (1974), S. Danishefsky *et al.*, ...102, 2838 (1980); 104, 7591 (1982).



...ystals, mp 210-211° (evac tube); racemate reported as ...37-238° (Tsuda) and mp 175-176° (Danishefsky). $[\alpha]_D^{25}$ ...3° (82 mg in 2 ml chloroform). Sol in methanol, ...ol, choroform. Sparingly sol in ether.
...drochloride, crystals, mp 206°, water soluble.
...hiodide, crystals, dec 220° (evacuated tube).

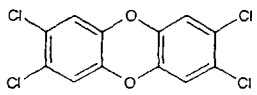
...51. Tazobactam. *[2S-(2α,3β,5α)]-3-Methyl-7-oxo-3-...2,3-triazol-1-ylmethyl)-4-thia-1-azabicyclo[3.2.0]hep-...arboxylic acid 4,4-dioxide;* 2β-[(1,2,3-triazol-1-yl)-...yl]-2α-methylpenam-3α-carboxylic acid 1,1-dioxide; ...330H; CL-298741. $C_{10}H_{11}N_4O_5S$; mol wt 300.30. C ...H 4.03%, N 18.66%, O 26.64%, S 10.68%. β-Lac- ...inhibitor. Prepn: R. G. Micetich *et al.*, Eur. pat. ...97,446; *eidem*, U.S. pat. 4,562,073 (1984, 1985 both ...no); R. G. Micetich *et al., J. Med. Chem.* 30, 1469 ... Degradation in solution: T. Marunaka *et al., Chem. ...Bull.* 36, 4478 (1988); in solid state: E. Matsushima ...*bid.* 4593. β-Lactamase inhibiting activity in com- ...with clavulanic acid and sulbactam, *q.q.v.*, vs aer- ...H. R. Jacobs *et al., Antimicrob. Ag. Chemother.* 29, ...986); vs anaerobes: P. C. Appelbaum *et al., ibid.* 30, ...HPLC determn in biological materials: T. Marunaka ...*Chromatog.* 431, 87 (1988). Clinical trial in combi- ...with piperacillin, *q.v.*: I. M. Gould *et al., Drugs Exp. ...Ex.* 17, 187 (1991).



...lium salt. $C_{10}H_{11}N_4NaO_5S$. *YTR-830, CL-307579.* ...phous solid, mp > 170° (dec).
...bination of sodium salt with piperacillin sodium. ...illine, *Tazocin, Zosyn.*

THERAP CAT: In combination with β-lactam antibiotics as antibacterial.

9252. TCDD. *2,3,7,8-Tetrachlorodibenzo[b,e][1,4]dioxin; 2,3,7,8-tetrachlorodibenzo-p-dioxin;* 2,3,6,7-tetrachlorodibenzodioxin; dioxin; TCDBD. $C_{12}H_4Cl_4O_2$; mol wt 321.97. C 44.77%, H 1.25%, Cl 44.04%, O 9.94%. Highly toxic contaminant; produced as a by-product during the manuf of chlorinated phenols (2,4,5-trichlorophenol, *q.v.*) and phenoxyherbicides (2,4-D and 2,4,5-T, *q.q.v.*), chlorine bleaching of paper pulp and combustion of chlorine-containing waste. Prepn: W. Sandermann, *Ber.* 90, 690 (1957); M. Tomita *et al., Yakugaku Zasshi* 79, 186 (1959), *C.A.* 53, 13152d (1959). Crystal structure: F. P. Boer *et al., Acta Crystallogr.* **28B**, 1023 (1972). Toxicity and metabolism: B. A. Schwetz *et al.*, in *Chlorodioxins-Origin and Fate*, E. H. Blair, Ed., *Advances in Chemistry Series* 120 (A.C.S., Washington, D.C., 1973) pp 55-69; A. Poland, A. Kende, *Fed. Proc.* 35, 2404 (1976). Environmental degradation: D. G. Crosby, A. S. Wong, *Science* 195, 1337 (1976). Comprehensive review of formation, chemistry, and toxic and environmental effects: *Chlorodioxins—Origin and Fate, loc. cit.* 141 pp; *Dioxin—Toxicological and Chemical Aspects*, F. Cattabeni *et al.*, Eds. (Wiley, New York, 1978) 222 pp; special issue, *Chem. & Eng. News* 61 (June 6, 1983). Review of toxicology and human exposure: *Toxicological Profile for 2,3,7,8-Tetradichlorodibenzo-p-dioxin* (PB89-214522, 1989) 135 pp; of receptor binding and mechanism of toxicity: J. P. Whitlock, Jr., *Ann. Rev. Pharmacol. Toxicol.* 30, 251-277 (1990); of epidemiological data: L. Tollefson, *Regul. Toxicol. Pharmacol.* 13, 150-169 (1991); of carcinogenicity: J. Huff *et al., Ann. Rev. Pharmacol. Toxicol.* 34, 343-372 (1994).



Needles, mp 295° (Tomita); crystals from anisole, mp 320-325° (Sandermann). LD_{50} in male, female rats (mg/kg): 0.022, 0.045 orally (Schwetz).

Note: An industrial accident during the manufacture of 2,4,5-trichlorophenol in Seveso, Italy on July 10, 1976 caused the release of an estimated two to ten pounds of TCDD into the environment. Concentrations as high as 51.3 ppm TCDD were found in some samples: R. Rawls, D. A. O'Sullivan, *Chem. & Eng. News* 54, 27 (Aug. 23, 1976); A. Hay, *Nature* 262, 636 (1976).

TCDD, as a contaminant created in the manufacture of *Agent Orange*, a widely used defoliant in Vietnam during the 1960's, has also been implicated as the causative agent of various symptoms described by veterans exposed to the defoliant, *see* C. Holden, *Science* 205, 770 (1979).

Caution: Toxic effects in animals include the wasting syndrome, gastric ulcers, immunotoxicity, hepatotoxicity, hepatoporphyria, vascular lesions, chloracne, teratogenicity, fetotoxicity, impaired reproductive performance, endometriosis and delayed death. Industrial workers exposed to TCDD have developed chloracne, porphyrinuria and porphyria cutanea tarda. *See* Poland, Kende, *loc. cit.*; C. D. Carter *et al., Science* 188, 738 (1975). This substance may reasonably be anticipated to be a carcinogen: *Seventh Annual Report on Carcinogens* (PB95-109781, 1994) p 369.

9253. Tebuconazole. *(±)-α-[2-(4-Chlorophenyl)ethyl]-α-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol; (RS)*-1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-pentan-3-ol; ethyltrianol; fenetrazole; terbuconazole; terbutrazole; BAY HWG 1608; HWG-1608; Corail; Elite; Folicur; Horizon; Lynx; Raxil; Silvacur. $C_{16}H_{22}ClN_3O$; mol wt 307.82. C 62.43%, H 7.20%, Cl 11.52%, N 13.65%, O 5.20%. Ergosterol biosynthesis inhibitor. Prepn: G. Holmwood *et al.*, Eur. pat. Appl. 40,345; *eidem*, U.S. pat. 4,723,-984 (1981, 1988 both to Bayer). Synthesis of enantiomers: J. Kaulen, *Agnew. Chem. Int. Ed. Engl.* 28, 462 (1989). Photodegradation: H. Wamhoff *et al.*, *Z. Naturforsch.* 49b, 280 (1994). GC determn in plant material, soil and water: W. Maasfeld, *Pflanzenschutz-Nachr. Bayer (Eng. Ed.)* 40, 29 (1987). Review of chemistry and biochemistry: D. Berg *et*

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U.S. PHARMACOPEIA

The Standard of Quality SM

PLAINTIFF'S EXHIBIT 20 CLEARY - 2/10/03

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Rockville, MD 20852
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Fax: (301) 816-8148
Web: www.usp.org
E-mail: custsvc@usp.org

Vital Statistics

Year Founded: 1820

Who We Are

USP IS AN INDEPENDENT, NON-GOVERNMENT, not-for-profit organization that promotes the public health by establishing state-of-the art standards and developing programs to ensure the quality of medicines and related healthcare technologies and practices.

A unique process of public involvement is central to USP's public health work and stewardship. Equally significant are the vital contributions of volunteers representing pharmacy, medicine, and other healthcare professions, as well as science, academia, the U.S. government, the pharmaceutical industry, and other consumer organizations.

Major Markets

USP STANDARDS ARE KNOWN WORLDWIDE as an assurance of high quality.

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USP–NF: The United States Pharmacopeia–National Formulary (USP–NF) is the FDA-recognized source for standards of identity, strength, quality, and purity for drug substances, dosage forms, excipients, and dietary supplements; tests and assays; and more. The latest annual edition, USP 26–NF 21, becomes official on January 1, 2003. USP–NF is available in print, online, intranet, and CD formats.

Reference Standards: USP Reference Standards are highly characterized specimens of drug substances, excipients, major impurities, degradation products, and performance calibrators. They are provided for use in compendial methodology. USP Reference Standards are established through an extensive process of collaborative laboratory testing among USP, FDA, and the pharmaceutical industry.

Pharmacopeial Forum: USP's Pharmacopeial Forum (PF) and PF Online complement USP–NF. PF and PF Online feature proposed revisions to USP–NF, as well as revisions that become official and binding before the next USP–NF edition is published. PF and PF Online also request public review and comment on proposed revisions.

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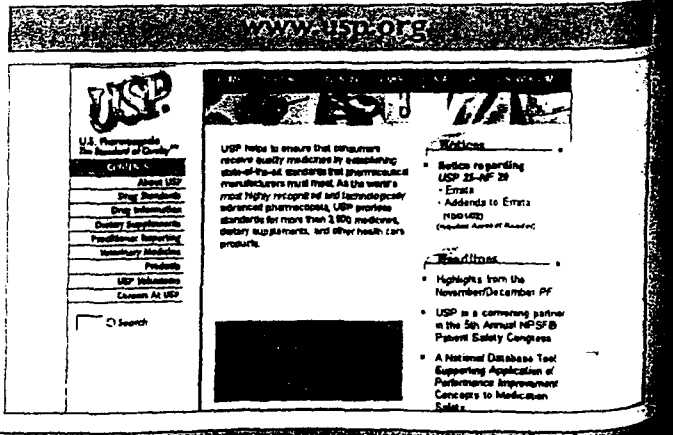
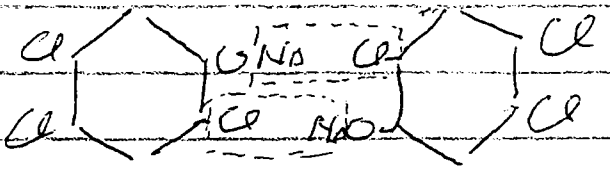
Medmarx Patient Safety Solutions: USP's Medmarx is a national medication error reporting database and system for data analysis designed to improve patient safety and reduce costs. More than 500 hospitals and health care organizations have enrolled and collectively have submitted over 300,000 anonymous medication error records, making it the largest database of its kind.



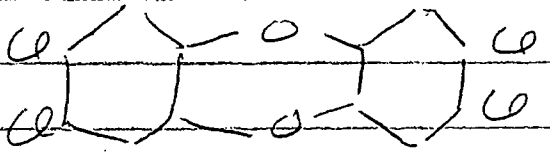
PLAINTIFF'S EXHIBIT 21 CLEARY-2/10/03

Notes

One doesn't need any chemistry to visualize how TCDD is formed when TCP, as its Sodium salt, is subjected to high temperature, >150°C



+ 2 NaCl
Sodium Chloride



TCDD

In the course of producing TCP from TCB, TCDD is formed to the extent of about 15-25 ppm in the TCP.

TCPAA (2,4,5-T) the herbicide used in "Agent Orange" was introduced into general use in the 50's, heavily used for controling brush along Roadways It was made (from crude TCP such as purchased by Metro-Atlantic) by the millions of pounds, by Monsanto, Dow, Thompson Chem (St. Louis) and Diamond Alkali, among others

The only "pure" TCP being

produced was by Hooker Chem. Co. of Niagara Falls who sold it exclusively to Givaudan for the production of Hexachlorophene. Hooker's waste went into "Love Canal"

All of the 2,4,5-T acquired for "Agent Orange" was made directly from the same solution form of crude TCP shipped to Centredale.

I have included herein several pages copied from Merck Index, Vol. XII which will help to elucidate the relationships among TCB, TCP, 2,4,5-T and TCDD.

TCB = 1,2,4,5-Tetrachlorobenzene
TCP = 2,4,5-Trichlorophenol
2,4,5-T = 2,4,5-Trichlorophenoxy-acetic Acid
TCDD = Dioxin*

*There are numerous other "Dioxins", this one being, purportedly, far more toxic than the others

Action/Use
ACTION: Volatile insecticide in controlled release strip formulation. Acts by fumigant action on trapped insects. Inner reservoir automatically replenishes the insecticide to maintain effective concentration in traps.
USE: For insect monitoring and mass trapping programs for control of boll weevil, codling moth, gypsy moth, spruce budworm, forest tent caterpillar, Mediterranean fruit fly, Oriental fruit fly, southwestern corn borer, and sweetpotato weevil. Used in conjunction with insect attractants to kill trapped insects. Increases trap and monitoring efficiency by reducing the number of escapees before and during counts; especially effective in non-sticky traps.
Safety Guidelines
SIGNAL WORD: CAUTION.
TOXICITY CLASS: III.
HANDLING AND STORAGE CAUTIONS: Do not open pouch until ready to use. Keep out of reach of children. Avoid contact with eyes, skin, and clothing. Always wash hands with soap and water after handling.
Emergency Guidelines
FIRE EXTINGUISHING MEDIA: CO_2, powder, foam. Use self-contained breathing apparatus.
ANTIDOTE: Atropine sulfate and 2-PAM.
FIRST AID: Get immediate medical aid. Eyes, wash with water for at least 15 minutes. Skin, wash with soap and water; remove contaminated clothing. Ingestion, induce vomiting. Inhalation, remove from exposure. Give oxygen if breathing labored.
EMERGENCY TELEPHONE: 717-764-1191 (Hercon Environmental Corp.).

Hercules 7531 — see Herban*.
Hercules 9573 — see Azak*.
Hercules 14503 — see Torak*.
Hercules AC 528 — see Dioxathion.
Hercules AC 5727 — see UC 10854.
Heritage* — see Azoxystrobin.
Herkol* — see Dichlorvos.

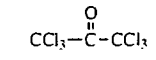
HETP

Chemistry
COMPOSITION: Ethyl polyphosphates containing 12-20% tetraethyl pyrophosphate. Also known as hexa-ethyl tetraphosphate.
Action/Use
ACTION: Insecticide.
USE: TEPP is the insecticidal component of HETP, and is the material now in production.
Safety Guidelines
HANDLING AND STORAGE CAUTIONS: HETP acts as a contact poison and hydrolyzes rapidly in aqueous solution. Therefore, sprays should be applied immediately after mixing. Absorbed rapidly through the skin of warm-blooded animals and inhalation of the vapors also may be dangerous. Possesses no phytotoxicity at normal concentrations.
See TEPP.

Hexablanc* Insecticide (BHC) — Discontinued by Rhone-Poulenc.

Hexachloroacetone

Identification
COMMON NAME: Hexachloroacetone (ISO); HCA (WSSA).
CODE NUMBERS: CAS 116-16-5; SHA 043701.
Chemistry
COMPOSITION: 1,1,1,3,3,3-hexachloro-2-propanone (CAS 8 and 9CI).



Hexachloroacetone

Action/Use
ACTION: Nonselective herbicide.
Safety Guidelines
SIGNAL WORD: CAUTION.
TOXICITY CLASS: III.
TOXICITY: (Rat): Oral LD_{50} 3550 mg/kg.

Hexachlorobenzene

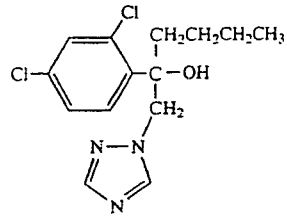
Identification
COMMON NAME: Hexachlorobenzene (ISO, BSI).
TRIVIAL NAME: HCB.
CODE NUMBERS: CAS 118-74-1; SHA 061001.
FORMULATORS' TRADE NAMES: No Bunt*.
DISCONTINUED NAMES: Anticarie*, Ceku C.B.* (Cequisa); Granero* (Atanor S.A.); Res-Q* (+ maneb + captan) (PBI/Gordon).
Chemistry
COMPOSITION: Hexachlorobenzene (IUPAC and CAS).
Action/Use
ACTION: Seed protectant.
Safety Guidelines
SIGNAL WORD: CAUTION.
TOXICITY CLASS: IV.
TOXICITY: (Rat): Oral LD_{50} 40,000 mg/kg. May cause slight irritation to skin.
Emergency Guidelines
FIRST AID: Get immediate medical aid. Ingestion, induce vomiting with warm salt water or syrup of Ipecac. Note: Some physicians may discourage use of saline emesis.

Hexachlorophene

Identification
COMMON NAME: Hexachlorophene (INN, USP, USAN); hexachlorophane (BAN).
EXP. CODE NUMBERS: G-11.
OTHER CODE NUMBERS: CAS 70-30-4; SHA 044901.
FORMULATORS' TRADE NAMES: Seribak*.
DISCONTINUED NAMES: Hexalint*, Hexaphene* L.V., Hexide*, Isobac*, Nabac* (Webb Wright Corp.).
Chemistry
COMPOSITION: 2,2'-methylenebis(3,4,6-trichlorophenol) (IUPAC).
Action/Use
ACTION: Broad spectrum contact soil, foliar fungicide.
Environmental Guidelines
HAZARDS: Bird: 575 mg/kg (bobwhite quail); 1450 mg/kg (mallard, female).
Safety Guidelines
SIGNAL WORD: CAUTION.
TOXICITY CLASS: III.
TOXICITY: (Rat): Oral LD_{50} 560 mg/kg.
HANDLING AND STORAGE CAUTIONS: May be fatal if swallowed. Do not get in eyes or on skin. Do not breathe spray mist.
Emergency Guidelines
FIRST AID: Get immediate medical aid. Eyes, flush with water. Skin, wash with soap and water. Ingestion, induce vomiting with warm salt water or syrup of Ipecac. Note: Some physicians may discourage use of saline emesis.

Hexaconazole

BP: Rallis India Ltd. (Contaf*)
ZENECA Agrochemicals (Anvil*, Planete Aster*)
Identification
COMMON NAME: Hexaconazole (ISO draft, ANSI, BSI).
CODE NUMBERS: CAS 79983-71-4.
FORMULATORS' TRADE NAMES: Canvil* (VAPCO).
Chemistry
COMPOSITION: (RS)-2-(2,4-dichlorophenyl)-1-(IH-1,2,4-triazol-1-yl)-hexan-2-ol (IUPAC).
PROPERTIES: White crystalline solid with no odor. Melting point 111°C. Soluble in a range of organic solvents.



Hexaconazole

Action/Use
ACTION: Fungicide.
USE: Controls powdery mildews, scabs and rusts of vines, pome fruits, vegetables, and major diseases of small grain cereals.
FORMULATIONS: Oil miscible liquid, soluble grain, suspension concentrate.
PREMIXES: Various Planete* premixes (+ carbendazim or chlorothalonil or fenpropidin) (ZENECA Agrochemicals).
Environmental Guidelines
SOLUBILITY: Low solubility in water.
Safety Guidelines
SIGNAL WORD: CAUTION.
TOXICITY CLASS: IV.
TOXICITY: (Rat): Oral LD_{50} 6071 mg/kg (female).
PROTECTIVE CLOTHING: Protective gloves and eye protection when handling concentrate.
HANDLING AND STORAGE CAUTIONS: Refer to individual formulations.

Hexadienyl Isobutyrate

BP: Agri-Pharm de Mexico, S.A. de C.V.

HESPERIDIN
ACTA PHARMACAL
• ASHLAND CHEMICAL COMPANY
DNP INTERNATIONAL CO., INC.
FREEMAN INDUSTRIES, L.L.C.
KADEN BIOCHEMICALS GMBH
KINGCHEM INC.
MAYPRO INDUSTRIES, INC.
Pharmline, Inc.
STAUBER PERFORMANCE INGREDIENTS, INC.
F. H. Taussig, Inc.
P. L. Thomas & Co., Inc.

HESPERIDIN COMPLEX
ARROW CHEMICAL INC.
• ASHLAND CHEMICAL COMPANY
Belmont Chemicals Inc.
• BOTANICALS INTERNATIONAL, INC., DIV. OF ZUELLIG BOTANICALS, INC.
CPB INTERNATIONAL, INC.
FREEMAN INDUSTRIES, L.L.C.
GENERICHEM CORP.
H. INTERDONATI, INC.
RIA International
SELTZER CHEMICALS, INC.
STAUBER PERFORMANCE INGREDIENTS, INC.

HESPERIDIN METHYL CHALCONE
FREEMAN INDUSTRIES, L.L.C.

HEXABROMOCYCLODODECANE
AMERIBROM INC.
★ BERJE INC.

1,2,5,6,9,10-HEXABROMOCYCLODODECANE
ALBEMARLE CORP. (FORMERLY ETHYL CHEMICALS GROUP)
Great Lakes Chemical Corp.

HEXACHLOROACETONE *See Hexachloro-2-Propanone*

HEXACHLORO CYCLOPENTADIENE
VELSICOL CHEMICAL CORP.

HEXACHLOROCYCLOTRIPHOSPHAZENE
ESPRIT CHEMICAL CO.

HEXACHLOROETHANE
FABRICHEM, INC.
HUMMEL CROTON INC.
Neuchem Inc.
Service Chemical, Inc.
Skyline International

HEXACHLOROPHENE
International Commodities Export Corp.
• SPECTRUM BULK CHEMICALS, DIVISION OF SPECTRUM QUALITY PRODUCTS, INC.

HEXACHLOROPHENE, DIOXIN-FREE
Inchema, Inc.

HEXACHLORO-2-PROPANONE (Hexachloroacetone)
WACKER CHEMICALS (USA), INC.
WACKER-CHEMIE GMBH

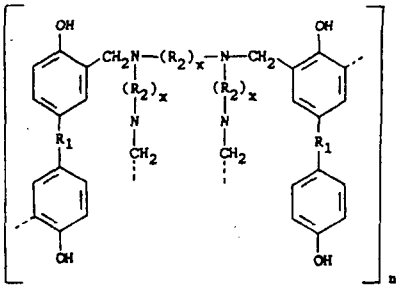
1H,1H,9H-HEXADECAFLUORO-1-NONANOL
OAKWOOD PRODUCTS

n-HEXADECANE
• SPECTRUM BULK CHEMICALS, DIVISION OF SPECTRUM QUALITY PRODUCTS, INC.

HEXADECANEDIOIC ACID
• SPECTRUM BULK CHEMICALS, DIVISION OF SPECTRUM QUALITY PRODUCTS, INC.

THERAP CAT: Poloxamer 182LF as pharmaceutic aid; 188 as cathartic.

7433. Polyamine-Methylene Resin. Resinat; Exorbin. Phenol condensation product with polyamines. An ion-exchange resin specially purified for medicinal use.



Light amber, granular, free-flowing powder. Insol in water, alcohol, ether, aq solns of acids and alkalies. Under the conditions of the old N.N.R. assay for acid-consuming capacity, not less than 50 ml 0.1 *N* hydrochloric acid is consumed by 0.2 g of the resin.

THERAP CAT: Antacid.

7434. Polybasite. $8Ag_2S.Sb_2S_3$—silver antimony sulfide.

7435. Polybenzarsol. *(4-Hydroxyphenyl)arsonic acid polymer with formaldehyde;* Benzodol. A polymeric mixture obtained by adding formaldehyde (40%) (0.116 mole) over a 3-hr period to *p*-hydroxybenzenearsonic acid (0.209 mole) in 180 g of 90% H_2SO_4 at 0-5° and keeping it cold for 21 hrs. Dilution of the mixture with H_2O precipitates the product: Faith, *J. Am. Chem. Soc.* **72,** 837 (1950). Description: Jones *et al., Antibiot. & Chemother.* **8,** 400 (1958).

White powder. Somewhat sol in water; sol in alcoholic NaOH. LD_{50} i.p. in mice: 235 mg/kg. No deaths after 4 g/kg i.g. in mice.

THERAP CAT: Antiprotozoal.

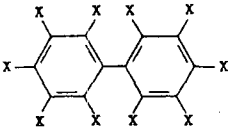
7436. Polybrominated Biphenyls. PBB's; brominated biphenyls; polybromobiphenyls. Mixtures with structures similar to polychlorinated biphenyls, *q.v.*, where each X = H or Br. Once widely used commercially. Prepn: H. Hahn *et al.*, Ger. pat. **1,161,547** (1964 to Chem. Fabrik Kalb); G. A. Burk, U.S. pat. **3,733,366** (1973 to Dow); L. C. Mitchell, D. R. Breckenridge, U.S. pats. **3,763,248** and **3,833,674** (1973, 1974 both to Ethyl Corp.). Persistence in soils: L. W. Jacobs *et al., J. Agr. Food Chem.* **24,** 1198 (1976). Photodegradation: L. O. Ruzo *et al., ibid.* 1062. Review of environmental hazards: K. Kay, *Environ. Res.* **13,** 74-93 (1977); F. J. DiCarlo *et al., Environ. Health Perspect.* **23,** 351-365 (1978).

Firemaster BP-6, major component is *2,2',4,4',5,5'-hexabromobiphenyl.* Softens at 72°, dec above 300°. Low vapor press; degraded by uv light. Very sol in benzene, toluene; insol in water.

Note: The 1973 "Michigan Incident" in which BP-6 was accidentally added to animal feed, and resulted in widespread destruction of contaminated farm animals, led to the removal of BP-6 from the market: L. J. Carter, *Science* **192,** 240 (1976).

USE: Flame retardant.

7437. Polychlorinated Biphenyls. PCBs; chlorinated biphenyls; chlorobiphenyls; Aroclor; Clophen; Fenclor; Kanechlor; Phenoclor; Pyralene; Santotherm. Once widely used industrial chemicals whose high stability contributed to both their commercial usefulness and their long-term deleterious environmental and health effects. Early synthesis: H. Schmidt, G. Schulz, *Ann.* **207,** 338 (1881). Commercially available since 1930: C. Penning, *Ind. Eng. Chem.* **22,** 1180 (1930). Commercial PCBs are mixtures. The Aroclors are characterized by four digit numbers. The first two digits indicate that the mixture contains biphenyls (12), triphenyls (54) or both (25, 44); the last two digits give the weight percent of chlorine in the mixture (e.g. Aroclor 1242 contains biphenyls with approx 42% chlorine). Reviews of environmental impact and toxicity: L. Fishbein, *Ann. Rev. Pharmacol.* **14,** 139-156 (1974); R. D. Kimbrough, *CRC Crit. Rev. Toxicol.* **2,** 445-498 (1974); *National Conference on Polychlorinated Biphenyls,* Nov. 19-21, 1975 (EPA-560/6-75-004, 1976) 487 pp. Accumulation of airborne PCBs in foliage: E. H. Buckley, *Science* **216,** 520 (1982). *Reviews:* H. L. Hubbard in *Kirk-Othmer Encyclopedia of Chemical Technology* vol. 5 (Interscience, New York, 2nd ed., 1964) pp 289-297; O. Hutzinger *et al., The Chemistry of PCB's* (CRC Press, Cleveland, Ohio, 1974) 269 pp; J. W. Lloyd *et al., J. Occup. Med.* **18,** 109-113 (1976). Review of carcinogenicity studies: *IARC Monographs* **18,** 43-103 (1978).



X = H or Cl

Aroclor 1242, clear, mobile liquid; av. number Cl/molecule: 3.10. d_4^{25} 1.381, d_4^{55} 1.392. Distillation range 325-366°. Flash point (open cup) 348-356°F. n_D^{20} 1.627-1.629. Dielectric constant (1000 cycles) 5.6 (25°), 4.9 (100°).

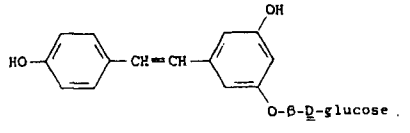
Aroclor 1254, light yellow, viscous liquid; av. number Cl/molecule: 4.96. d_4^{65} 1.495; d_4^{55} 1.505. Distillation range 365-390°. No open cup flash point to boiling. n_D^{20} 1.629-1.641. Dielectric constant (1000 cycles) 5.0 (25°), 4.3 (100°). LD_{50} orally in weanling rats: 1295 mg/kg, Kimbrough, *loc. cit.*

Aroclor 1260, light yellow, soft, sticky resin; av. number Cl/molecule: 6.30. d_4^{90} 1.555; d_4^{55} 1.566. Distillation range 385-420. No open cup flash point to boiling. n_D^{20} 1.647-1.649. Dielectric constant (1000 cycles) 4.3 (25°); 3.7 (100°). LD_{50} orally in weanling rats: 1315 mg/kg, Kimbrough, *loc. cit.*

Caution: Toxic effects in humans include chloracne, pigmentation of skin and nails, excessive eye discharge, swelling of eyelids, distinctive hair follicles, gastrointestinal disturbances. In Japan, accidental contamination of rice bran oil with Kanneclor 400 led to an outbreak of what became known as "Yusho disease", *see* M. Kuratsune *et al.*, in EPA-560/6-75-004, *loc. cit.*, p 14. Toxic symptoms in animals include hepatocellular carcinoma, hypertrophy of the liver, adenofibrosis, weight and hair loss, mouth and eyelid edema, acneform lesions, decreased hemoglobin + hematocrit, gastric mucosal ulceration and reduced ability to reproduce. These substances have been listed as carcinogens by the EPA: *Second Annual Report on Carcinogens* (NTP 81-43, Dec. 1981) pp 206-209.

USE: In electrical capacitors, electrical transformers, vacuum pumps, gas-transmission turbines. Formerly used in U.S. as hydraulic fluids, plasticizers, adhesives, fire retardants, wax extenders, dedusting agents, pesticide extenders, inks, lubricants, cutting oils, in heat transfer systems, carbonless reproducing paper.

7438. Polydatin. *3-Hydroxy-5-[2-(4-hydroxyphenyl)ethenyl]phenyl-β-D-glucopyranoside; 3-hydroxy-5-(p-hydroxystyryl)phenyl glucoside;* 3,4',5-trihydroxystilbene-3-β-D-glucoside; resveratrol-3-β-mono-D-glucoside; piceid. $C_{20}H_{22}O_8$; mol wt 390.40. C 61.53%, H 5.68%, O 32.79%. Isoln from fresh root of *Polygonum cuspidatum* Sieb. & Zucc., *Polygonaceae,* and structure: Nonomura *et al., Yakugaku Zasshi* **83,** 988 (1963).



Trihydrate, crystals, mp 225-226°. $[\alpha]_D^{27}$ −74.9° (c = 1.709 in ethanol).

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9450. 1,1,2-Trichloroethane. Vinyl trichloride. $C_2H_3Cl_3$; mol wt 133.42. C 18.00%, H 2.27%, Cl 79.73%. CH_2Cl-$CHCl_2$. Prepd by catalytic chlorination of ethane or ethylene: Joseph, U.S. pat. 2,752,401 and Pye, U.S. pat. 2,752,402 (both 1956 to Dow); Reynolds, U.S. pat. 2,783,286 (1957 to Olin Mathieson).

Nonflammable liquid; pleasant odor; d_4^{20} 1.4416; solidif −35°; bp 113-114°; n_D^{20} 1.4711. Insol in water; misc with alcohol, ether, and many other organic liquids. LD_{50} orally in rats: 0.58 ml/kg, H. F. Smyth *et al., Am. Ind. Hyg. Assoc. J.* **30,** 470 (1969).

USE: Solvent for fats, waxes, natural resins, alkaloids. *Caution:* Irritating to eyes, mucous membranes, and, in high concns, narcotic.

9451. 2,2,2-Trichloroethanol. Trichloroethyl alcohol. $C_2H_3Cl_3O$; mol wt 149.42. C 16.08%, H 2.02%, Cl 71.19%, O 10.71%. CCl_3CH_2OH. Prepd by reduction of the corresponding ester, acid chloride, or acid with lithium aluminum hydride: Sroog *et al., J. Am. Chem. Soc.* **71,** 1710 (1949). Manufacture by reduction of chloral hydrate with an amine borane: Chamberlain, Schechter, U.S. pat. 2,898,379 (1959 to Callery Chem.).

Hygroscopic liquid, ethereal odor. At low temps it crystallizes in rhombic tablets. mp at 18°; bp 151-153°; d_{20}^{20} 1.55. Sol in about 12 parts water; miscible with alcohol or ether. pH of aq soln is 5-6, but on prolonged contact with water some free acid is formed. *Keep well closed and protected from light.* LD_{50} orally in rats: 600 mg/kg, *Handbook of Toxicology* vol. 1, W. S. Spector, Ed. (Saunders, Philadelphia, 1955) pp 302-303.

THERAP CAT: Hypnotic, anesthetic.

9452. Trichloroethylene. *Trichloroethene;* ethinyl trichloride; Tri-Clene; Trielene; Trilene; Trichloran; Trichloren; Algylen; Trimar; Triline; Tri; Trethylene; Westrosol; Chlorylen; Gemalgene; Germalgene. C_2HCl_3; mol wt 131.40. C 18.28%, H 0.77%, Cl 80.95%. $CCl_2{=}CHCl$. Usually prepd from *sym*-tetrachloroethane by elimination of HCl (by boiling with lime): Ger. pat. 171,900. By passing tetrachloroethane vapor over $CaCl_2$ catalyst at 300°: Ger. pat. 263,457; without catalyst at 450-470°: Brit. pat. 575,530 (1946 to du Pont). Review of mfg processes: S. A. Miller, *Chem. Process Eng.* 47, 268 (1966); Faith, Keyes & Clark's *Industrial Chemicals,* F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 844-848. Toxicity and metabolism: E. Browning, *Toxicity and Metabolism of Industrial Solvents* (Elsevier, New York, *1965*) pp *189-212.*

Nonflammable, mobile liquid. Characteristic odor resembling that of chloroform. d_4^4 1.4904; d_4^{15} 1.4695; d_4^{20} 1.4649. Vapor density: 4.53 (air = 1.00). Solidifies at −84.8°. bp_{760} 86.7°; bp_{400} 67.0°; bp_{200} 48.0°; bp_{100} 31.4°; bp_{60} 20.0°; bp_{20} −1.0°; bp_{10} −12.4°; bp_5 −22.8°; $bp_{1.0}$ −43.8°; n_D^{17} 1.47914; n_D^{25} 1.45560. Practically insol in water; misc with ether, alcohol, chloroform. Dissolves most fixed and volatile oils. Slowly dec (with formn of HCl) by light in the presence of moisture. Trichloroethylene for medicinal purposes may contain some thymol or ammonium carbonate (not more than 20 mg/100 ml) as a stabilizer. Industrial grades of trichloroethylene may contain other stabilizers such as triethanolamine stearate and cresol. LD_{50} orally in rats: 4.92 ml/kg; LC (4 hrs) in rats: 8000 ppm, Smyth *et al., Am. Ind. Hyg. Assoc. J.* **30,** 470 (1969).

Caution: Use with adequate ventilation. Preserve trichloroethylene in sealed, light-resistant ampuls or in frangible, light-resistant glass tubes. Avoid prolonged exposure of the product to excessive heat. It must be dispensed in the unopened glass container in which it was placed by the manufacturer.

Human Toxicity: Moderate exposures can cause symptoms similar to alcohol inebriation. Higher concns can have narcotic effect. Deaths occurring after heavy exposure have been attributed to ventricular fibrillation. Liver injury is not definitely established in occupational exposures. Found to induce hepatocellular carcinomas in National Cancer Institute tests on mice: *Chem. & Eng. News* 54, 4 (Apr. 5, 1976).

USE: Solvent for fats, waxes, resins, oils, rubber, paints, and varnishes. Solvent for cellulose esters and ethers. Used for solvent extraction in many industries. In degreasing, in dry cleaning. In the manuf of organic chemicals, pharmaceuticals, such as chloroacetic acid.

THERAP CAT: Analgesic (inhalation).

THERAP CAT (VET): Inhalant anesthetic.

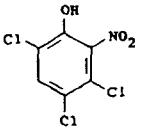
9453. Trichlorofluoromethane. Trichloromonofluoromethane; fluorotrichloromethane; Freon 11; Frigen 11; Arcton 9. CCl_3F; mol wt 137.38. C 8.74%, Cl 77.43%, F 13.83%. Prepn: Henne, *Organic Reactions* 2, 64 (1944). Manuf: Faith, Keyes & Clark's *Industrial Chemicals,* F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 325-330.

Liquid at temps below 23.7°. Faint ethereal odor. Nonflammable. $d_4^{17.2}$ 1.494; d_{gas}^{25} 5.04 (air = 1). mp −111°. bp_{760} 23.7°; bp_{400} +6.8°; bp_{200} −9.1°; bp_{100} −23.0°; bp_{60} −32.3°; bp_{40} −39.0°; bp_{20} −49.7°; bp_{10} −59.0°; bp_5 −67.6°; $bp_{1.0}$ −84.3°. Crit temp 198°; crit press. 43.2 atm (635 lb/sq inch. abs). $n_D^{18.5}$ 1.3865. Dipole moment 0.45. Practically insol in water. Sol in alcohol, ether, other, organic solvents. Less toxic than carbon dioxide, but decomposes into harmful materials by flames or high heat.

USE: In refrigeration machinery requiring a refrigerant effective at negative pressures. As aerosol propellant. *Caution:* May be narcotic in high concentrations.

Note: Consult latest Government regulations on use as aerosol propellant.

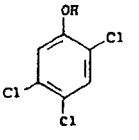
9454. 3,4,6-Trichloro-2-nitrophenol. 2-Nitro-3,4,6-trichlorophenol; 2,4,5-trichloro-6-nitrophenol; Dowlap. $C_6H_2Cl_3NO_3$; mol wt 242.44. C 29.72%, H 0.83%, Cl 43.87%, N 5.78%, O 19.80%. Prepd by dissolving 2,4,5-trichlorophenol in glacial acetic acid and treating with concd nitric acid: Kohn, Fink, *Monatsh.* **58,** 73 (1931); Harrison *et al., J. Chem. Soc.* **1943,** 235.



Pale yellow crystals from petr ether, mp 92-93°.

USE: To combat the sea lamprey, an eel-like fish which attacks trout, especially in the Great Lakes region.

9455. 2,4,5-Trichlorophenol. Collunosol; Dowicide 2. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, H 1.53%, O 8.10%, Cl 53.87%. Prepd by treating 1,2,4,5-tetrachlorobenzene with methanolic NaOH in autoclave at 160° for several hrs: Harrison *et al., J. Chem. Soc.* **1943,** 235; Agfa, Ger. pat. **411,052** (1925); *Chem. Zentr.* **1925, I,** 2411.



Needles from alcohol or ligroin. Strong phenolic odor. mp 67°. Sublimes. bp_{746} 248°. bp_{760} 253°. Weak monobasic acid. K at 25° = 4.3 × 10^{-6}. Soly (g/100 g of solvent at 25°): acetone 615; benzene 163; carbon tetrachloride 51; ether 525; denatured alcohol formula 30, 525; methanol 615; liquid petrolatum (at 50°) 56; soybean oil 79; toluene 122; water <0.2. LD_{50} orally in rats: 0.82 g/kg, Deichmann, *Fed. Proc.* 2, 76 (1943).

Sodium salt sesquihydrate, *Dowicide B.* Flakes [prepd according to U.S. pat. 1,991,329 (1935 to Dow)]. Solubility (g/100 g solvent at 25°): acetone 163; denatured alcohol formula 30, 186; ethylene glycol 33; methanol 241; water 113. pH of satd aq soln 11.0-13.0.

Complex with triisobutyl phosphate, $C_{18}H_{30}ClO_5P$, *Trichlorex.* Prepn: Bouillenne-Wallrand *et al.,* Fr. pat. M149 (1961 to Pechiney). Liquid. $bp_{0.01}$ 94-103°.

USE: Fungicide, bactericide.

9456. 2,4,6-Trichlorophenol. Dowicide 2S; Omal. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, O 8.10%, H 1.53%, Cl

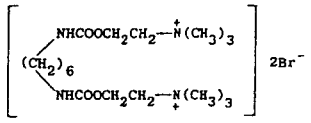
L - This would repel more than half a pound for a 150 lb man.

USE: As reagent for pyrophosphoric acid, for the estimation of phosphate.

4571. Hexaborane(10). Hexaboron decahydride; borohexane. B_6H_{10}; mol wt 75.00. B 86.56%, H 13.44%. Prepd by the reaction of magnesium boride with hydrochloric or phosphoric acid: Stock, Kuss, *Ber.* **56B**, 789 (1923).

Liquid. mp −62.3°; bp 108°; vapor pressure (0°): 7.5 mm: Burg, Kratzer, *Inorg. Chem.* **1**, 725 (1962). d^0 0.69. Slowly dec at room temp. Hydrolyzes in water after long heating.

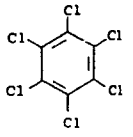
4572. Hexacarbacholine Bromide. ***2,2'-[1,6-Hexanediylbis(iminocarbonyloxy)]bis[N,N,N-trimethylethanaminium] dibromide;*** choline bromide hexamethylenedicarbamate; hexamethylenedicarbamic acid choline bromide diester; hexamethylene-1,6-bis(carbamoylcholine bromide); *N,N'*-hexamethylenebis[(2-carbamoyloxyethyl)trimethylammonium bromide]; BC 16; Imbretil. $C_{18}H_{40}Br_2N_4O_4$; mol wt 536.38. C 40.31%, H 7.52%, Br 29.80%, N 10.45%, O 11.93%. Preparation: Schmied *et al.*, **Austrian pat. 185,371** (1956); Ger. pat. **1,021,842** (1958 to Oesterreichische Stickstoffwerke).



Crystals from ethanol, mp 174-176°.

THERAP CAT: Skeletal muscle relaxant.

4573. Hexachlorobenzene. Perchlorobenzene; Anticarie; Bunt-cure; Bunt-no-more; Julin's carbon chloride. C_6Cl_6; mol wt 284.80. C 25.30%, Cl 74.70%. Not to be confused with benzene hexachloride, *see* Lindane. Prepn: Becke, Sperber, **U.S. pat. 2,792,434** (1957 to BASF). Teratogenicity studies: K. D. Courtney *et al., Toxicol. Appl. Pharmacol.* **35**, 239 (1976). Carcinogenicity studies: J. R. P. Cabral *et al., Nature* **269**, 510 (1977).



Needles. d^{23} 2.044. mp 231°. bp 323-326°. Vapor press at 20°: 1.09 × 10^{-5} mm Hg. Sublimable. Insol in water; sparingly sol in cold alcohol; sol in benzene, chloroform, ether. LD_{50} orally in rats: 10,000 mg/kg, *RTECS* Vol. I, R. J. Lewis, R. L. Tatken, Eds. (1979) p 216.

USE: In organic syntheses. Fungicide. *Caution:* Cutaneous porphyria may result from prolonged periods of ingestion, R. Ockner, R. Schmid, *Nature* **189**, 499 (1961).

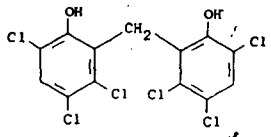
4574. Hexachloroethane. Carbon hexachloride; perchloroethane. C_2Cl_6; mol wt 236.74. C 10.15%, Cl 89.85%. CCl_3CCl_3. Prepn: *Beilstein* **1**, 87 (1918) and suppls.

Crystals; camphoraceous odor. d 2.09. Readily sublimes without melting. bp 186.8° (triple point). Heat of sublimation 12.2 kcal/mol. Sol in alcohol, benzene, chloroform, ether, oils. Insol in water. MLD i.v. in dogs: 325 mg/kg, Barsoum, Saad, *Quart. J. Pharm. Pharmacol.* 7, 205 (1934).

USE: Solvent; in explosives; as camphor substitute in celluloid; rubber vulcanizing accelerator. *Caution:* May be moderately irritating to skin, mucous membranes.

THERAP CAT (VET): Anthelmintic (flukicide).

4575. Hexachlorophene. ***2,2'-Methylenebis[3,4,6-trichlorophenol];*** 2,2'-dihydroxy-3,3',5,5',6,6'-hexachlorodiphenylmethane; bis(3,5,6-trichloro-2-hydroxyphenyl)methane; G-11; AT-7; Bilevon; Dermadex; Exofene; Gamophen; Hexosan; pHisohex; Surgi-Cen; Surofene. $C_{13}H_6Cl_6O_2$; mol wt 406.92. C 38.37%, H 1.49%, Cl 52.28%, O 7.86%. Prepd by the condensation of 2 mols of 2,4,5-trichlorophenol with 1 mol formaldehyde in the presence of concd sulfuric acid: Gump, **U.S. pat. 2,250,480** (1941 to Burton T. Bush). Improved procedures: **U.S. pat. 2,435,593** (1948) and **2,812,365** (1957 to Givaudan).



Crystals from benzene, mp 164-165°. Practically insol in water; sol in alcohol, acetone, ether, chloroform, propylene glycol; polyethylene glycols; olive oil; cottonseed oil; dil aq solns of the alkalies. Forms salts with alkalies and alkaline earths. Phenol coefficient ~125 (monopotassium salt). Incompatible with Tweens from bacteriological point of view.

Monophosphate, *Hepadist.*

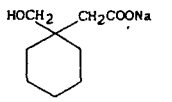
Toxicity: Excessive dosage to animals results in symptoms of neurotoxicity. Reversible vacuolar changes mainly affecting the myelin of the brain and spinal cord have been reported. Because of potential neurotoxicity in humans, the FDA has regulated use. *See* Lockhart, *Pediatrics* **50**, 229 (1972).

USE: Chiefly in the manuf of germicidal soaps.

THERAP CAT: Anti-infective, topical; detergent.

THERAP CAT (VET): Anthelmintic (flukicide).

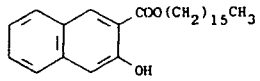
4576. Hexacyclonate Sodium. ***1-(Hydroxymethyl)cyclohexaneacetic acid sodium salt;*** sodium 3,3-pentamethylene-4-hydroxybutyrate; sodium β,β-pentamethylene-γ-hydroxybutyrate; β,β-pentamethylene-γ-hydroxybutyric acid sodium salt; Gevilon; Neuryl. $C_9H_{15}NaO_3$; mol wt 194.21. C 55.66%, H 7.78%, Na 11.84%, O 24.71%. Prepn: Van Wessem, Sakal; Shavel *et al.*, **U.S. pats. 2,960,441; 3,007,940** (1960; 1961 to Warner-Lambert).



Monohydrate, platelets from *n*-butanol + benzene, mp 106-108°. The anhydr salt is hygroscopic. Readily sol in water, methanol, ethanol; sparingly sol in ether, acetone.

THERAP CAT: Central stimulant.

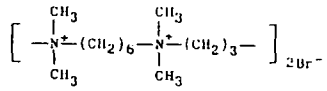
4577. Hexadecyl 3-Hydroxy-2-naphthoate. ***3-Hydroxy-2-naphthalenecarboxylic acid hexadecyl ester.*** $C_{27}H_{40}O_3$; mol wt 412.59. C 78.59%, H 9.77%, O 11.63%. Prepd by the action of 3-hydroxy-2-naphthoyl chloride on cetyl alc: Oshima, Hayashi, *J. Soc. Chem. Ind. Japan* **44**, 821 (1941).



Greenish-white, flaky crystals, mp 72-73°. Soluble in benzene, glacial acetic acid, petr ether. Sparingly sol in cold alcohol. Insol in water.

USE: As waterproofing agent for rayon.

4578. Hexadimethrine Bromide. ***N,N,N',N'-Tetramethyl-1,6-hexanediamine polymer with 1,3-dibromopropane;*** polymer of *N,N,N',N'*-tetramethylhexamethylenediamine and trimethylene bromide; poly(*N,N,N',N'*-tetramethyl-*N*-trimethylenehexamethylenediammonium dibromide); Polybrene. $(C_{13}H_{30}Br_2N_2)_x$.



White, hygroscopic, amorphous polymer. Soluble in water up to 10%. pH of 1% saline soln 5-9. Stable in soln and when autoclaved. Polymers with mol wt of 5000-10,000 have LD_{50} i.v. in mice of 25-40 mg/kg. Ref: Kimura *et al., Toxicol. Appl. Pharmacol.* **1**, 185 (1959).

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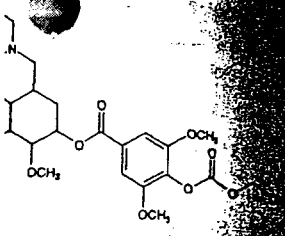
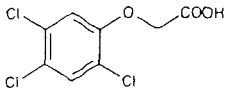


9194. 2,4,5-T. *(2,4,5-Trichlorophenoxy)acetic acid;* Esteron 245; Trioxone; Weedone. $C_8H_5Cl_3O_3$; mol wt 255.48. C 37.61%, H 1.97%, Cl 41.63%, O 18.79%. Post-emergence herbicide. Prepd from 2,4,5-trichlorophenol: Pokorny, *J. Am. Chem. Soc.* 63, 1768 (1941); from benzenehexachloride: Dalal, *ibid.* 74, 3890 (1952). Activity: C. L. Hamner, T. B. Sabry, *Science* 100, 154 (1944). Contains trace levels of TCDD, *q.v.*, as a contaminant: J. Smith, *Science* 203, 1090 (1979); *Chem. & Eng. News* 59, 6 (Jan. 5, 1981). Toxicity: W. A. Rowe, T. A. Hymas, *Am. J. Vet. Res.* 15, 622 (1954). See also 2,4-D.



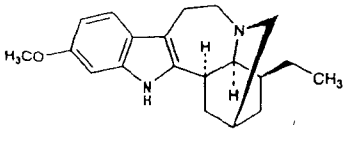
Crystals from benzene, mp 153°. d_{20}^{20} 1.80. Soly in water at 30°: 238 mg/kg. Sol in alcohol. Forms water-soluble sodium and alkanolamine salts. Commercial products are usually in the form of amines or esters, often in mixture with 2,4-D. LD_{50} orally in mice, rats: 389, 500 mg/kg (Rowe, Hymas).

Caution: Potential symptoms of overexposure in animals are ataxia; skin irritation, acne-like rash. *See NIOSH Pocket Guide to Chemical Hazards* (DHHS/NIOSH 90-117, 1990) p 302.

Note: In March 1985 the E.P.A. terminated all registrations for the use of this herbicide on rice fields, orchards, sugarcane, rangeland and other noncrop sites. This follows the 1970 action of the Department of Agriculture halting the use of the pesticide on all food crops except rice: Chem. & Eng. News 63, 6 (Mar. 25, 1985).

USE: Formerly as herbicide.

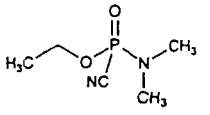
9195. Tabernanthine. *13-Methoxyibogamine.* $C_{20}H_{26}N_2O$; mol wt 310.44. C 77.38%, H 8.44%, N 9.02%, O 5.15%. Indole alkaloid isolated from root of *Tabernanthe iboga* Baill., *Apocynaceae:* Delourme-Houdé, *Ann. Pharm. Franc.* 4, 30 (1946); Dickel *et al., J. Am. Chem. Soc.* 80, 123 (1958). Also in *Tabernaemontana* and *Stemmadenia* spp.; usually found in ibogaine mother liquors: Walls *et al., Lloydia* 21, 173 (1958). Isoln from genus *Conopharingia, Apocynaceae:* Renner, Prins, U.S. pat. 3,008,954 (1961 to Ciba). Structure: Bartlett *et al., J. Am. Chem. Soc.* 80, 126 (1958), Mass spectrum: Biemann, Friedmann-Spiteller, *ibid.* 83, 4805 (1961). Derivs: Taylor, U.S. pat. 2,877,229 (1959 to Ciba). Interaction with benzodiazepine receptors: M. L. Trouvin *et al., Eur. J. Pharmacol.* 140, 303 (1987).



Needles or shiny leaflets from ethanol, mp 213.5-215°. Sublimes at 160° (0.005 mm pressure). $[\alpha]_D^{20}$ −40° (acetone). pKa 6.04 in 80% methylcellosolve. uv max (ethanol): 228, 299 nm (log ε 4.53, 3.64, 3.77). Sol in alcohol, benzene, ether, chloroform. Practically insol in water.

Hydrochloride, $C_{20}H_{26}N_2O.HCl$, crystals from water, dec 277°. $[\alpha]_D^{25}$ −66° (methanol, Dickel, *loc. cit.*); mp 210°, $[\alpha]_D$ −76.5° (methanol, Delourme-Houdé). Sol in water. More sol in chloroform than ibogaine hydrochloride.

9196. Tabun. *Dimethylphosphoramidocyanidic acid, ethyl ester;* ethyl *N*-dimethylphosphoramidocyanidate; dimethylamidoethoxyphosphoryl cyanide; GA. $C_5H_{11}N_2O_2P$; mol wt 162.13. C 37.04%, H 6.84%, N 17.28%, O 19.74%, P 19.10%. Military nerve gas; prepd from dimethylamidophosphoryl dichloride and sodium cyanide in the presence of ethanol: Holmstedt, *Acta Physiol. Scand.* 25, Suppl. 90, 14 (1951). The synthesis of dimethylamidophosphoryl dichloride is also described by Michaelis, *Ann.* 326, 129 (1903). Alternate synthetic route: B. C. Saunders, *Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine* (Cambridge, 1957) p 91. Toxicity study: B. Holmstedt, *Pharmacol. Rev.* 11, 567 (1959). Brief review: Schrader, *Die Entwicklung neuer insektizider Phosphorsaüre-Ester* (Verlag Chemie, Weinheim, 1963) p 3.

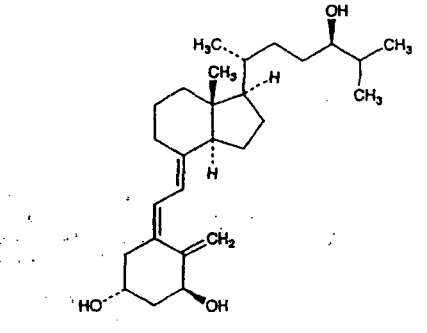


Liquid. Fruity odor reminiscent of bitter almonds. d 1.077. mp −50°. bp_{760} 240°; bp_{10} 120°; bp_9 100-108°. n_D^{20} 1.4250. IR absorption: *Acta Chem. Scand.* 5, 1179 (1951). Readily sol in organic solvents. Miscible with water, but quickly hydrolyzed. Bleaching powder (chlorinated lime) destroys Tabun, but gives rise to cyanogen chloride. *Extremely poisonous!* LD_{50} i.p. in mice: 0.6 mg/kg (Holmstedt). The lethal dose for man may be as low as 0.01 mg/kg, *Chem. & Eng. News* 31, 4676 (1953).

Caution: Potent cholinesterase inhibitor. Toxic not only by inhalation but by absorption through skin and eyes. Inhalation produces constriction of pupils of the eye, difficulty in breathing followed by bronchial constriction, convulsions, death.

USE: Chemical warfare agent.

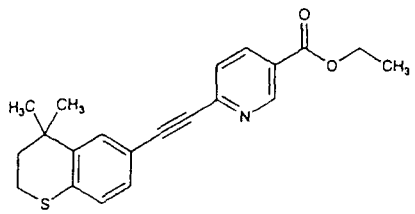
9197. Tacalcitol. *(1α,3β-5Z,7E,24R)-9,10-Secocholesta-5,7,10(19)-triene-1,3,24-triol;* 1α,24(*R*)-dihydroxycholecalciferol; 1α,24*R*-dihydroxyvitamin D_3; TV-02; Bonalfa. $C_{27}H_{44}O_3$; mol wt 416.64. C 77.84%, H 10.64%, O 11.52%. Bioactive, synthetic vitamin D_3 analog; exhibits antiproliferative effect on keratinocytes. Prepn: T. Takeshita *et al.*, Ger. pat. 2,526,981; *eidem*, U.S. pat. 4,022,891 (1976, 1977 both to Teijin); M. Morisaki *et al., J. Chem. Soc, Perkin Trans. I* 1975, 1421; K. Ochi *et al., ibid.* 1979, 165. Pharmacology: T. Matsunage *et al., J. Dermatol.* 17, 135 (1990). Clinical evaluation in psoriasis: M. J. P. Gerritsen *et al., Brit. J. Dermatol.* 131, 57 (1994). *Review:* M. Nishimura *et al., Eur. J. Dermatol.* 3, 255-261 (1993).



White solid. uv max (ethanol): 265 nm.

THERAP CAT: Antipsoriatic.

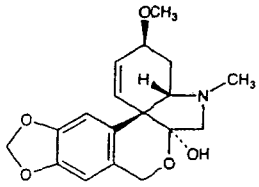
9198. Tachysterol. *(3β,6E,22E)-9,10-Secoergosta-5(10),6,8,22-tetraen-3-ol.* $C_{28}H_{44}O$; mol wt 396.66. C 84.79%, H 11.18%, O 4.03%. From ergosterol or lumisterol by ultraviolet irradiation: Windaus *et al., Ann.* 492, 226 (1932); *Ann.* 499, 188 (1932); Dimroth, *Ber.* 70, 1631 (1937). From calciferol by adsorption on acid clay: Thibaudet, *Compt. Rend.* 220, 751 (1945). From precalciferol: Velluz, Goffinet, U.S. pat. 2,847,426 (1958 to UCLAF). Structure: Grundmann, *Z. Physiol. Chem.* 252, 151 (1938); Thibaudet, *loc. cit.* Stereochemistry of the tachysterol system: Inhoffen, *Ber.* 88, 1424 (1955); Verloop, *Rec. Trav. Chim.* 76, 689 (1957); Delaroff *et al., Bull. Soc. Chim. France* 1963, 1739.



White solid.

THERAP CAT: Antiacne; antipsoriatic.

9250. Tazettine. Sekisanine; sekisanoline; ungernine. $C_{18}H_{21}NO_5$; mol wt 331.37. C 65.24%, H 6.39%, N 4.23%, O 24.14%. From *Narcissus tazetta* L., *Lycoris radiata* Herb., *Ungernia sewerzowi* (Rgl.) Fedtsch., and other *Amaryllidaceae*: Späth, Kahovec, *Ber.* 67, 1501 (1934). Structure and stereochemistry: Ikeda *et al., J. Chem. Soc.* 1956, 4749. Abs config: Highet, Highet, *Tetrahedron Letters* 1966, 4099. Synthesis: Hendrickson *et al., J. Am. Chem. Soc.* 92, 5538 (1970); Tsuda *et al., Tetrahedron Letters* 1972, 3153. Biosynthesis: Fales, Wildman, *J. Am. Chem. Soc.* 86, 294 (1964). Identity with sekisanine and sekisanoline: Ikeda *et al.; loc. cit.* Stereospecific total synthesis: Hendrickson *et al., J. Am. Chem. Soc.* 96, 7781 (1974); S. Danishefsky *et al., ibid.* 102, 2838 (1980); 104, 7591 (1982).

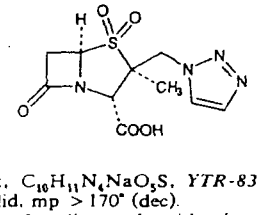


Crystals, mp 210-211° (evac tube); racemate reported as mp 237-238° (Tsuda) and mp 175-176° (Danishefsky). $[\alpha]_D^{25}$ +150.3° (82 mg in 2 ml chloroform). Sol in methanol, ethanol, choroform. Sparingly sol in ether.

Hydrochloride, crystals, mp 206°, water soluble.

Methiodide, crystals, dec 220° (evacuated tube).

9251. Tazobactam. *[2S-(2α,3β,5α)]-3-Methyl-7-oxo-3-(1H-1,2,3-triazol-1-ylmethyl)-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid 4,4-dioxide;* 2β-[(1,2,3-triazol-1-yl)-methyl]-2α-methylpenam-3α-carboxylic acid 1,1-dioxide; YTR-830H; CL-298741. $C_{10}H_{12}N_4O_5S$; mol wt 300.30. C 40.00%, H 4.03%, N 18.66%, O 26.64%, S 10.68%. β-Lactamase inhibitor. Prepn: R. G. Micetich *et al.*, Eur. pat. Appl. 97,446; *eidem*, U.S. pat. 4,562,073 (1984, 1985 both to Taiho); R. G. Micetich *et al., J. Med. Chem.* 30, 1469 (1987). Degradation in solution: T. Marunaka *et al., Chem. Pharm. Bull.* 36, 4478 (1988); in solid state: E. Matsushima *et al., ibid.* 4593. β-Lactamase inhibiting activity in comparison with clavulanic acid and sulbactam, *q.q.v.*, vs aerobes: M. R. Jacobs *et al., Antimicrob. Ag. Chemother.* 29, 780 (1986); vs anaerobes: P. C. Appelbaum *et al., ibid.* 30, 789. HPLC determn in biological materials: T. Marunaka *et al., J. Chromatog.* 431, 87 (1988). Clinical trial in combination with piperacillin, *q.v.*: I. M. Gould *et al., Drugs Exp. Clin. Res.* 17, 187 (1991).

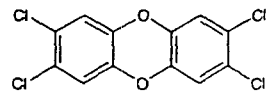


Sodium salt, $C_{10}H_{11}N_4NaO_5S$, *YTR-830, CL-307579.* Amorphous solid, mp > 170° (dec).

Combination of sodium salt with piperacillin sodium, *Tazocilline, Tazocin, Zosyn.*

THERAP CAT: In combination with β-lactam antibiotics as antibacterial.

9252. TCDD. *2,3,7,8-Tetrachlorodibenzo[b,e][1,4]dioxin; 2,3,7,8-tetrachlorodibenzo-p-dioxin;* 2,3,6,7-tetrachlorodibenzodioxin; dioxin; TCDBD. $C_{12}H_4Cl_4O_2$; mol wt 321.97. C 44.77%, H 1.25%, Cl 44.04%, O 9.94%. Highly toxic contaminant; produced as a by-product during the manuf of chlorinated phenols (2,4,5-trichlorophenol, *q.v.*) and phenoxyherbicides (2,4-D and 2,4,5-T, *q.q.v.*), chlorine bleaching of paper pulp and combustion of chlorine-containing waste. Prepn: W. Sandermann, *Ber.* 90, 690 (1957); M. Tomita *et al., Yakugaku Zasshi* 79, 186 (1959), *C.A.* 53, 13152d (1959). Crystal structure: F. P. Boer *et al., Acta Crystallogr.* 28B, 1023 (1972). Toxicity and metabolism: B. A. Schwetz *et al.*, in *Chlorodioxins-Origin and Fate*, E. H. Blair, Ed., *Advances in Chemistry Series* 120 (A.C.S., Washington, D.C., 1973) pp 55-69; A. Poland, A. Kende, *Fed. Proc.* 35, 2404 (1976). Environmental degradation: D. G. Crosby, A. S. Wong, *Science* 195, 1337 (1976). Comprehensive review of formation, chemistry, and toxic and environmental effects: *Chlorodioxins—Origin and Fate, loc. cit.* 141 pp; *Dioxin—Toxicological and Chemical Aspects*, F. Cattabeni *et al.*, Eds. (Wiley, New York, 1978) 222 pp; special issue, *Chem. & Eng. News* 61 (June 6, 1983). Review of toxicology and human exposure: *Toxicological Profile for 2,3,7,8-Tetradichlorodibenzo-p-dioxin* (PB89-214522, 1989) 135 pp; of receptor binding and mechanism of toxicity: J. P. Whitlock, Jr., *Ann. Rev. Pharmacol. Toxicol.* 30, 251-277 (1990); of epidemiological data: L. Tollefson, *Regul. Toxicol. Pharmacol.* 13, 150-169 (1991); of carcinogenicity: J. Huff *et al., Ann. Rev. Pharmacol. Toxicol.* 34, 343-372 (1994).



Needles, mp 295° (Tomita); crystals from anisole, mp 320-325° (Sandermann). LD_{50} in male, female rats (mg/kg): 0.022, 0.045 orally (Schwetz).

Note: An industrial accident during the manufacture of 2,4,5-trichlorophenol in Seveso, Italy on July 10, 1976 caused the release of an estimated two to ten pounds of TCDD into the environment. Concentrations as high as 51.3 ppm TCDD were found in some samples: R. Rawls, D. A. O'Sullivan, *Chem. & Eng. News* 54, 27 (Aug. 23, 1976); A. Hay, *Nature* 262, 636 (1976).

TCDD, as a contaminant created in the manufacture of *Agent Orange*, a widely used defoliant in Vietnam during the 1960's, has also been implicated as the causative agent of various symptoms described by veterans exposed to the defoliant, *see* C. Holden, *Science* 205, 770 (1979).

Caution: Toxic effects in animals include the wasting syndrome, gastric ulcers, immunotoxicity, hepatotoxicity, hepatoporphyria, vascular lesions, chloracne, teratogenicity, fetotoxicity, impaired reproductive performance, endometriosis and delayed death. Industrial workers exposed to TCDD have developed chloracne, porphyrinuria and porphyria cutanea tarda. *See* Poland, Kende, *loc. cit.*; C. D. Carter *et al., Science* 188, 738 (1975). This substance may reasonably be anticipated to be a carcinogen: *Seventh Annual Report on Carcinogens* (PB95-109781, 1994) p 369.

9253. Tebuconazole. *(±)-α-[2-(4-Chlorophenyl)ethyl]-α-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol; (RS)-*1-(4-chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-pentan-3-ol; ethyltrianol; fenetrazole; terbuconazole; terbutrazole; BAY HWG 1608; HWG-1608; Corail; Elite; Folicur; Horizon; Lynx; Raxil; Silvacur. $C_{16}H_{22}ClN_3O$; mol wt 307.82. C 62.43%, H 7.20%, Cl 11.52%, N 13.65%, O 5.20%. Ergosterol biosynthesis inhibitor. Prepn: G. Holmwood *et al.*, Eur. pat. Appl. 40,345; *eidem*, U.S. pat. 4,723,984 (1981, 1988 both to Bayer). Synthesis of enantiomers: J. Kaulen, *Agnew. Chem. Int. Ed. Engl.* 28, 462 (1989). Photodegradation: H. Wamhoff *et al., Z. Naturforsch.* 49b, 280 (1994). GC determn in plant material, soil and water: W. Maasfeld, *Pflanzenschutz-Nachr. Bayer (Eng. Ed.)* 40, 29 (1987). Review of chemistry and biochemistry: D. Berg *et*

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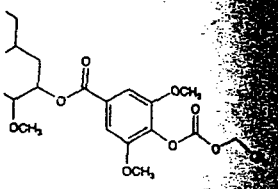
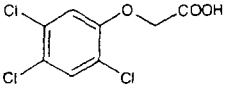


9194. 2,4,5-T. *(2,4,5-Trichlorophenoxy)acetic acid;* Esteron 245; Trioxone; Weedone. $C_8H_5Cl_3O_3$; mol wt 255.48. C 37.61%, H 1.97%, Cl 41.63%, O 18.79%. Post-emergence herbicide. Prepd from 2,4,5-trichlorophenol: Pokorny, *J. Am. Chem. Soc.* **63**, 1768 (1941); from benzenehexachloride: Hoist, *ibid.* **74**, 3890 (1952). Activity: C. L. Hamner, T. B. Tabey, *Science* **100**, 154 (1944). Contains trace levels of TCDD, *q.v.*, as a contaminant: J. Smith, *Science* **203**, 1090 (1979); *Chem. & Eng. News* **59**, 6 (Jan. 5, 1981). Toxicity: T. A. Rowe, T. A. Hymas, *Am. J. Vet. Res.* **15**, 622 (1954). *See also* 2,4-D.



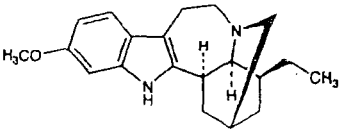
Crystals from benzene, mp 153°. d_{20}^{20} 1.80. Soly in water at 30°: 238 mg/kg. Sol in alcohol. Forms water-soluble sodium and alkanolamine salts. Commercial products are usually in the form of amines or esters, often in mixture with 2,4-D. LD_{50} orally in mice, rats: 389, 500 mg/kg (Rowe, Hymas).

Caution: Potential symptoms of overexposure in animals are ataxia; skin irritation, acne-like rash. *See NIOSH Pocket Guide to Chemical Hazards* (DHHS/NIOSH 90-117, 1990) p 202.

Note: In March 1985 the E.P.A. terminated all registrations for the use of this herbicide on rice fields, orchards, sugarcane, rangeland and other noncrop sites. This follows a 1970 action of the Department of Agriculture halting the use of the pesticide on all food crops except rice: Chem. & Eng. News 63, 6 (Mar. 25, 1985).

USE: Formerly as herbicide.

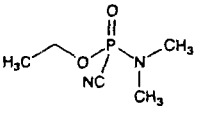
9195. Tabernanthine. *13-Methoxyibogamine.* $C_{20}H_{26}N_2O$; mol wt 310.44. C 77.38%, H 8.44%, N 9.02%, O 5.15%. Indole alkaloid isolated from root of *Tabernanthe iboga* Baill., *Apocynaceae:* Delourme-Houdé, *Ann. Pharm. franç.* **4**, 30 (1946); Dickel *et al., J. Am. Chem. Soc.* **80**, 123 (1958). Also in *Tabernaemontana* and *Stemmadenia* spp.; usually found in ibogaine mother liquors: Walls *et al., Tetrahedron* **2**, 173 (1958). Isoln from genus *Conopharingia, Apocynaceae:* Renner, Prins, U.S. pat. 3,008,954 (1961 to Ciby). Structure: Bartlett *et al., J. Am. Chem. Soc.* **80**, 126 (1958). Mass spectrum: Biemann, Friedmann-Spiteller, *ibid.* **83**, 4805 (1961). Derivs: Taylor, U.S. pat. 2,877,229 (1959 to Ciba). Interaction with benzodiazepine receptors: J. H. Trouvin *et al., Eur. J. Pharmacol.* **140**, 303 (1987).



Needles or shiny leaflets from ethanol, mp 213.5-215°. Sublimes at 160° (0.005 mm pressure). $[\alpha]_D^{20}$ −40° (acetone). pKa 6.04 in 80% methylcellosolve. uv max (ethanol): 228, 292, 299 nm (log ε 4.53, 3.64, 3.77). Sol in alcohol, benzene, ether, chloroform. Practically insol in water.

Hydrochloride, $C_{20}H_{26}N_2O.HCl$, crystals from water, dec 275-277°. $[\alpha]_D^{25}$ −66° (methanol, Dickel, *loc. cit.*); mp 210°, $[\alpha]_D$ −76.5° (methanol, Delourme-Houdé). Sol in water. More sol in chloroform than ibogaine hydrochloride.

9196. Tabun. *Dimethylphosphoramidocyanidic acid, ethyl ester;* ethyl *N*-dimethylphosphoramidocyanidate; dimethylamidoethoxyphosphoryl cyanide; GA. $C_5H_{11}N_2O_2P$; mol wt 162.13. C 37.04%, H 6.84%, N 17.28%, O 19.74%, P 19.10%. Military nerve gas; prepd from dimethylamidophosphoryl dichloride and sodium cyanide in the presence of ethanol: Holmstedt, *Acta Physiol. Scand.* **25**, Suppl. 90, 26 (1951). The synthesis of dimethylamidophosphoryl dichloride is also described by Michaelis, *Ann.* **326**, 129 (1903). Alternate synthetic route: B. C. Saunders, *Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine* (Cambridge, 1957) p 91. Toxicity study: B. Holmstedt, *Pharmacol. Rev.* **11**, 567 (1959). Brief review: Schrader, *Die Entwicklung neuer insektizider Phosphorsaüre-Ester* (Verlag Chemie, Weinheim, 1963) p 3.

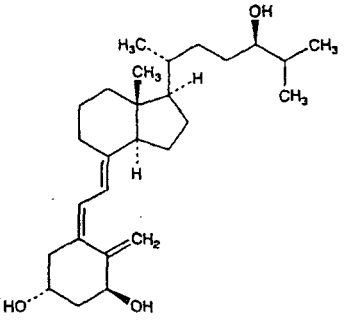


Liquid. Fruity odor reminiscent of bitter almonds. d 1.077. mp −50°. bp_{760} 240°; bp_{10} 120°; bp_9 100-108°. n_D^{20} 1.4250. IR absorption: *Acta Chem. Scand.* **5**, 1179 (1951). Readily sol in organic solvents. Miscible with water, but quickly hydrolyzed. Bleaching powder (chlorinated lime) destroys Tabun, but gives rise to cyanogen chloride. *Extremely poisonous!* LD_{50} i.p. in mice: 0.6 mg/kg (Holmstedt). The lethal dose for man may be as low as 0.01 mg/kg, *Chem. & Eng. News* **31**, 4676 (1953).

Caution: Potent cholinesterase inhibitor. Toxic not only by inhalation but by absorption through skin and eyes. Inhalation produces constriction of pupils of the eye, difficulty in breathing followed by bronchial constriction, convulsions, death.

USE: Chemical warfare agent.

9197. Tacalcitol. *(1α,3β-5Z,7E,24R)-9,10-Secocholesta-5,7,10(19)-triene-1,3,24-triol;* 1α,24(*R*)-dihydroxycholecalciferol; 1α,24*R*-dihydroxyvitamin D_3; TV-02; Bonalfa. $C_{27}H_{44}O_3$; mol wt 416.64. C 77.84%, H 10.64%, O 11.52%. Bioactive, synthetic vitamin D_3 analog; exhibits antiproliferative effect on keratinocytes. Prepn: T. Takeshita *et al., Ger. pat.* **2,526,981**; *eidem, U.S. pat.* **4,022,891** (1976, 1977 both to Teijin); M. Morisaki *et al., J. Chem. Soc. Perkin Trans. I* **1975**, 1421; K. Ochi *et al., ibid.* **1979**, 165. Pharmacology: T. Matsunage *et al., J. Dermatol.* **17**, 135 (1990). Clinical evaluation in psoriasis: M. J. P. Gerritsen *et al., Brit J. Dermatol.* **131**, 57 (1994). *Review:* M. Nishimura *et al., Eur. J. Dermatol.* **3**, 255-261 (1993).



White solid. uv max (ethanol): 265 nm.

THERAP CAT: Antipsoriatic.

9198. Tachysterol. *(3β,6E,22E)-9,10-Secoergosta-5(10),6,8,22-tetraen-3-ol.* $C_{28}H_{44}O$; mol wt 396.66. C 84.79%, H 11.18%, O 4.03%. From ergosterol or lumisterol by ultraviolet irradiation: Windaus *et al., Ann.* **492**, 226 (1932); *Ann.* **499**, 188 (1932); Dimroth, *Ber.* **70**, 1631 (1937). From calciferol by adsorption on acid clay: Thibaudet, *Compt. Rend.* **220**, 751 (1945). From precalciferol: Velluz, Goffinet, U.S. pat. **2,847,426** (1958 to UCLAF). Structure: Grundmann, *Z. Physiol. Chem.* **252**, 151 (1938); Thibaudet, *loc. cit.* Stereochemistry of the tachysterol system: Inhoffen, *Ber.* **88**, 1424 (1955); Verloop, *Rec. Trav. Chim.* **76**, 689 (1957); Delaroff *et al., Bull. Soc. Chim. France* **1963**, 1739.

9450. 1,1,2-Trichloroethane. Vinyl trichloride. $C_2H_3Cl_3$; mol wt 133.42. C 18.00%, H 2.27%, Cl 79.73%. CH_2Cl-$CHCl_2$. Prepd by catalytic chlorination of ethane or ethylene: Joseph, U.S. pat. **2,752,401** and Pye, U.S. pat. **2,752,402** (both 1956 to Dow); Reynolds, U.S. pat. **2,783,286** (1957 to Olin Mathieson).

Nonflammable liquid; pleasant odor; d_4^{20} 1.4416; solidif −35°; bp 113-114°; n_D^{20} 1.4711. Insol in water; misc with alcohol, ether, and many other organic liquids. LD_{50} orally in rats: 0.58 ml/kg, H. F. Smyth *et al., Am. Ind. Hyg. Assoc. J.* **30,** 470 (1969).

USE: Solvent for fats, waxes, natural resins, alkaloids. *Caution:* Irritating to eyes, mucous membranes, and, in high concns, narcotic.

9451. 2,2,2-Trichloroethanol. Trichloroethyl alcohol. $C_2H_3Cl_3O$; mol wt 149.42. C 16.08%, H 2.02%, Cl 71.19%, O 10.71%. CCl_3CH_2OH. Prepd by reduction of the corresponding ester, acid chloride, or acid with lithium aluminum hydride: Sroog *et al., J. Am. Chem. Soc.* 71, 1710 (1949). Manufacture by reduction of chloral hydrate with an amine borane: Chamberlain, Schechter, U.S. pat. **2,898,379** (1959 to Callery Chem.).

Hygroscopic liquid, ethereal odor. At low temps it crystallizes in rhombic tablets. mp at 18°; bp 151-153°; d_{20}^{20} 1.55. Sol in about 12 parts water; miscible with alcohol or ether. pH of aq soln is 5-6, but on prolonged contact with water some free acid is formed. *Keep well closed and protected from light.* LD_{50} orally in rats: 600 mg/kg, *Handbook of Toxicology* **vol. 1,** W. S. Spector, Ed. (Saunders, Philadelphia, 1955) pp 302-303.

THERAP CAT: Hypnotic, anesthetic.

9452. Trichloroethylene. *Trichloroethene;* ethinyl trichloride; Tri-Clene; Trielene; Trilene; Trichloran; Trichloren; Algylen; Trimar; Triline; Tri; Trethylene; Westrosol; Chlorylen; Germalgene; Germalgene. C_2HCl_3; mol wt 131.40. C 18.28%, H 0.77%, Cl 80.95%. $ClCl_2$=$CHCl$. Usually prepd from *sym*-tetrachloroethane by elimination of HCl (by boiling with lime): **Ger. pat. 171,900.** By passing tetrachloroethane vapor over $CaCl_2$ catalyst at 300°: **Ger. pat. 263,457;** without catalyst at 450-470°: **Brit. pat. 575,530** (1946 to du Pont). Review of mfg processes: S. A. Miller, *Chem. Process Eng.* **47,** 268 (1966); Faith, Keyes & Clark's *Industrial Chemicals,* F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 844-848. Toxicity and metabolism: E. Browning, *Toxicity and Metabolism of Industrial Solvents* (Elsevier, New York, 1965) pp 189-212.

Nonflammable, mobile liquid. Characteristic odor resembling that of chloroform. d_4^4 1.4904; d_4^{15} 1.4695; d_4^{20} 1.4649. Vapor density: 4.53 (air = 1.00). Solidifies at −84.8°. bp_{760} 86.7°; bp_{400} 67.0°; bp_{200} 48.0°; bp_{100} 31.4°; bp_{60} 20.0°; bp_{20} −1.0°; bp_{10} −12.4°; bp_5 −22.8°; $bp_{1.0}$ −43.8°; n_D^{17} 1.47914; n_D^{25} 1.45560. Practically insol in water; misc with ether, alcohol, chloroform. Dissolves most fixed and volatile oils. Slowly dec (with formn of HCl) by light in the presence of moisture. Trichloroethylene for medicinal purposes may contain some thymol or ammonium carbonate (not more than 20 mg/100 ml) as a stabilizer. Industrial grades of trichloroethylene may contain other stabilizers such as triethanolamine stearate and cresol. LD_{50} orally in rats: 4.92 ml/kg; LC (4 hrs) in rats: 8000 ppm, Smyth *et al., Am. Ind. Hyg. Assoc. J.* **30,** 470 (1969).

Caution: Use with adequate ventilation. Preserve trichloroethylene in sealed, light-resistant ampuls or in frangible, light-resistant glass tubes. Avoid prolonged exposure of the product to excessive heat. It must be dispensed in the unopened glass container in which it was placed by the manufacturer.

Human Toxicity: Moderate exposures can cause symptoms similar to alcohol inebriation. Higher concns can have narcotic effect. Deaths occurring after heavy exposure have been attributed to ventricular fibrillation. Liver injury is not definitely established in occupational exposures. Found to induce hepatocellular carcinomas in National Cancer Institute tests on mice: *Chem. & Eng. News* 54, 4 (Apr. 5, 1976).

USE: Solvent for fats, waxes, resins, oils, rubber, paints, and varnishes. Solvent for cellulose esters and ethers. Used for solvent extraction in many industries. In degreasing, in dry cleaning. In the manuf of organic chemicals, pharmaceuticals, such as chloroacetic acid.

THERAP CAT: Analgesic (inhalation).

THERAP CAT (VET): Inhalant anesthetic.

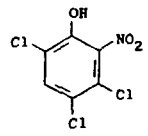
9453. Trichlorofluoromethane. Trichloromonofluoromethane; fluorotrichloromethane; Freon 11; Frigen 11; Arcton 9. CCl_3F; mol wt 137.38. C 8.74%, Cl 77.43%, F 13.83%. Prepn: Henne, *Organic Reactions* **2,** 64 (1944). Manuf: Faith, Keyes & Clark's *Industrial Chemicals,* F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 325-330.

Liquid at temps below 23.7°. Faint ethereal odor. Nonflammable. $d_4^{17.2}$ 1.494; d_{gas}^{25} 5.04 (air = 1). mp −111°. bp_{760} 23.7°; bp_{400} +6.8°; bp_{200} −9.1°; bp_{100} −23.0°; bp_{60} −32.3°; bp_{40} −39.0°; bp_{20} −49.7°; bp_{10} −59.0°; bp_5 −67.6°; $bp_{1.0}$ −84.3°. Crit temp 198°; crit press. 43.2 atm (635 lb/sq inch, abs). $n_D^{18.5}$ 1.3865. Dipole moment 0.45. Practically insol in water. Sol in alcohol, ether, other, organic solvents. Less toxic than carbon dioxide, but decomposes into harmful materials by flames or high heat.

USE: In refrigeration machinery requiring a refrigerant effective at negative pressures. As aerosol propellant. *Caution:* May be narcotic in high concentrations.

Note: Consult latest Government regulations on use as aerosol propellant.

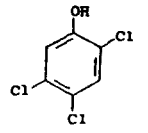
9454. 3,4,6-Trichloro-2-nitrophenol. 2-Nitro-3,4,6-trichlorophenol; 2,4,5-trichloro-6-nitrophenol; Dowlap. $C_6H_2Cl_3NO_3$; mol wt 242.44. C 29.72%, H 0.83%, Cl 43.87%, N 5.78%, O 19.80%. Prepd by dissolving 2,4,5-trichlorophenol in glacial acetic acid and treating with concd nitric acid: Kohn, Fink, *Monatsh.* **58,** 73 (1931); Harrison *et al., J. Chem. Soc.* **1943,** 235.



Pale yellow crystals from petr ether, mp 92-93°.

USE: To combat the sea lamprey, an eel-like fish which attacks trout, especially in the Great Lakes region.

9455. 2,4,5-Trichlorophenol. Collunosol; Dowicide 2. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, H 1.53%, O 8.10%, Cl 53.87%. Prepd by treating 1,2,4,5-tetrachlorobenzene with methanolic NaOH in autoclave at 160° for several hrs: Harrison *et al., J. Chem. Soc.* **1943,** 235; Agfa, Ger. pat. **411,052** (1925); *Chem. Zentr.* **1925, I,** 2411.



Needles from alcohol or ligroin. Strong phenolic odor. mp 67°. Sublimes. bp_{745} 248°. bp_{760} 253°. Weak monobasic acid. K at 25° = 4.3 × 10^{-8}. Soly (g/100 g of solvent at 25°): acetone 615; benzene 163; carbon tetrachloride 51; ether 525; denatured alcohol formula 30, 525; methanol 615; liquid petrolatum (at 50°) 56; soybean oil 79; toluene 122; water <0.2. LD_{50} orally in rats: 0.82 g/kg, Deichmann, *Fed. Proc.* **2,** 76 (1943).

Sodium salt sesquihydrate, *Dowicide B.* Flakes [prepd according to U.S. pat. **1,991,329** (1935 to Dow)]. Solubility (g/100 g solvent at 25°): acetone 163; denatured alcohol formula 30, 186; ethylene glycol 33; methanol 241; water 113. pH of satd aq soln 11.0-13.0.

Complex with triisobutyl phosphate, $C_{18}H_{30}ClO_5P$, *Trichlorex.* Prepn: Bouillenne-Wallrand *et al.,* Fr. pat. **M149** (1961 to Pechiney). Liquid. $bp_{0.01}$ 94-103°.

USE: Fungicide, bactericide.

9456. 2,4,6-Trichlorophenol. Dowicide 2S; Omal. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, O 8.10%, H 1.53%, Cl

9450. 1,1,2-Trichloroethane. Vinyl trichloride. $C_2H_3Cl_3$; mol wt 133.42. C 18.00%, H 2.27%, Cl 79.73%. CH_2Cl-$CHCl_2$. Prepd by catalytic chlorination of ethane or ethylene: Joseph, U.S. pat. 2,752,401 and Pye, U.S. pat. 2,752,402 (both 1956 to Dow); Reynolds, U.S. pat. 2,783,286 (1957 to Olin Mathieson).

Nonflammable liquid; pleasant odor; d_4^{20} 1.4416; solidif −35°; bp 113-114°; n_D^{20} 1.4711. Insol in water; misc with alcohol, ether, and many other organic liquids. LD_{50} orally in rats: 0.58 ml/kg, H. F. Smyth *et al., Am. Ind. Hyg. Assoc. J.* 30, 470 (1969).

USE: Solvent for fats, waxes, natural resins, alkaloids. *Caution:* Irritating to eyes, mucous membranes, and, in high concns, narcotic.

9451. 2,2,2-Trichloroethanol. Trichloroethyl alcohol. $C_2H_3Cl_3O$; mol wt 149.42. C 16.08%, H 2.02%, Cl 71.19%, O 10.71%. CCl_3CH_2OH. Prepd by reduction of the corresponding ester, acid chloride, or acid with lithium aluminum hydride: Sroog *et al., J. Am. Chem. Soc.* 71, 1710 (1949). Manufacture by reduction of chloral hydrate with an amine borane: Chamberlain, Schechter, U.S. pat. 2,898,379 (1959 to Callery Chem.).

Hygroscopic liquid, ethereal odor. At low temps it crystallizes in rhombic tablets, mp at 18°; bp 151-153°; d_{20}^{20} 1.55. Sol in about 12 parts water; miscible with alcohol or ether. pH of aq soln is 5-6, but on prolonged contact with water some free acid is formed. *Keep well closed and protected from light.* LD_{50} orally in rats: 600 mg/kg, *Handbook of Toxicology* vol. 1, W. S. Spector, Ed. (Saunders, Philadelphia, 1955) pp 302-303.

THERAP CAT: Hypnotic, anesthetic.

9452. Trichloroethylene. *Trichloroethene;* ethinyl trichloride; Tri-Clene; Trielene; Trilene; Trichloran; Trichloren; Algylen; Trimar; Triline; Tri; Trethylene; Westrosol; Chlorylen; Gemalgene; Germalgene. C_2HCl_3; mol wt 131.40. C 18.28%, H 0.77%, Cl 80.95%. $ClCl_2$=CHCl. Usually prepd from *sym*-tetrachloroethane by elimination of HCl (by boiling with lime): Ger. pat. 171,900. By passing tetrachloroethane vapor over $CaCl_2$ catalyst at 300°: Ger. pat. 263,457; without catalyst at 450-470°: Brit. pat. 575,530 (1946 to du Pont). Review of mfg processes: S. A. Miller, *Chem. Process Eng.* 47, 268 (1966); Faith, Keyes & Clark's *Industrial Chemicals*, F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 844-848. Toxicity and metabolism: E. Browning, *Toxicity and Metabolism of Industrial Solvents* (Elsevier, New York, 1965) pp 189-212.

Nonflammable, mobile liquid. Characteristic odor resembling that of chloroform. d_4^4 1.4904; d_4^{15} 1.4695; d_4^{20} 1.4649. Vapor density: 4.53 (air = 1.00). Solidifies at −84.8°. bp_{760} 86.7°; bp_{400} 67.0°; bp_{200} 48.0°; bp_{100} 31.4°; bp_{60} 20.0°; bp_{20} −1.0°; bp_{10} −12.4°; bp_5 −22.8°; $bp_{1.0}$ −43.8°; n_D^{17} 1.47914; n_D^{25} 1.45560. Practically insol in water; misc with ether, alcohol, chloroform. Dissolves most fixed and volatile oils. Slowly dec (with formn of HCl) by light in the presence of moisture. Trichloroethylene for medicinal purposes may contain some thymol or ammonium carbonate (not more than 20 mg/100 ml) as a stabilizer. Industrial grades of trichloroethylene may contain other stabilizers such as triethanolamine stearate and cresol. LD_{50} orally in rats: 4.92 ml/kg; LC (4 hrs) in rats: 8000 ppm, Smyth *et al., Am. Ind. Hyg. Assoc. J.* 30, 470 (1969).

Caution: Use with adequate ventilation. Preserve trichloroethylene in sealed, light-resistant ampuls or in frangible, light-resistant glass tubes. Avoid prolonged exposure of the product to excessive heat. It must be dispensed in the unopened glass container in which it was placed by the manufacturer.

Human Toxicity: Moderate exposures can cause symptoms similar to alcohol inebriation. Higher concns can have narcotic effect. Deaths occurring after heavy exposure have been attributed to ventricular fibrillation. Liver injury is not definitely established in occupational exposures. Found to induce hepatocellular carcinomas in National Cancer Institute tests on mice: *Chem. & Eng. News* 54, 4 (Apr. 5, 1976).

USE: Solvent for fats, waxes, resins, oils, rubber, paints, and varnishes. Solvent for cellulose esters and ethers. Used for solvent extraction in many industries. In degreasing, in dry cleaning. In the manuf of organic chemicals, pharmaceuticals, such as chloroacetic acid.

THERAP CAT: Analgesic (inhalation).

THERAP CAT (VET): Inhalant anesthetic.

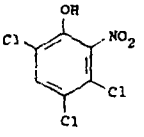
9453. Trichlorofluoromethane. Trichloromonofluoromethane; *fluorotrichloromethane;* Freon 11; Frigen 11; Arcton 9. CCl_3F; mol wt 137.38. C 8.74%, Cl 77.43%, F 13.83%. Prepn: Henne, *Organic Reactions* 2, 64 (1944). Manuf: Faith, Keyes & Clark's *Industrial Chemicals*, F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 325-330.

Liquid at temps below 23.7°. Faint ethereal odor. Nonflammable. $d_4^{17.2}$ 1.494; d_{25}^{25} 5.04 (air = 1). mp −111°. bp_{760} 23.7°; bp_{400} +6.8°; bp_{200} −9.1°; bp_{100} −23.0°; bp_{60} −32.3°; bp_{40} −39.0°; bp_{20} −49.7°; bp_{10} −59.0°; bp_5 −67.6°; $bp_{1.0}$ −84.3°. Crit temp 198°; crit press. 43.2 atm (635 lb/sq inch, abs). $n_D^{18.5}$ 1.3865. Dipole moment 0.45. Practically insol in water. Sol in alcohol, ether, other, organic solvents. Less toxic than carbon dioxide, but decomposes into harmful materials by flames or high heat.

USE: In refrigeration machinery requiring a refrigerant effective at negative pressures. As aerosol propellant. *Caution:* May be narcotic in high concentrations.

Note: Consult latest Government regulations on use as aerosol propellant.

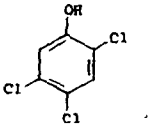
9454. 3,4,6-Trichloro-2-nitrophenol. 2-Nitro-3,4,6-trichlorophenol; *2,4,5-trichloro-6-nitrophenol;* Dowlap. $C_6H_2Cl_3NO_3$; mol wt 242.44. C 29.72%, H 0.83%, Cl 43.87%, N 5.78%, O 19.80%. Prepd by dissolving 2,4,5-trichlorophenol in glacial acetic acid and treating with concd nitric acid: Kohn, Fink, *Monatsh.* 58, 73 (1931); Harrison *et al., J. Chem. Soc.* 1943, 235.



Pale yellow crystals from petr ether, mp 92-93°.

USE: To combat the sea lamprey, an eel-like fish which attacks trout, especially in the Great Lakes region.

9455. 2,4,5-Trichlorophenol. Collunosol; Dowicide 2. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, H 1.53%, O 8.10%, Cl 53.87%. Prepd by treating 1,2,4,5-tetrachlorobenzene with methanolic NaOH in autoclave at 160° for several hrs: Harrison *et al., J. Chem. Soc.* 1943, 235; Agfa, Ger. pat. 411,052 (1925); *Chem. Zentr.* 1925, I, 2411.



Needles from alcohol or ligroin. Strong phenolic odor. mp 67°. Sublimes. bp_{746} 248°. bp_{760} 253°. Weak monobasic acid. K at 25° = 4.3×10^{-8}. Soly (g/100 g of solvent at 25°): acetone 615; benzene 163; carbon tetrachloride 51; ether 525; denatured alcohol formula 30, 525; methanol 615; liquid petrolatum (at 50°) 56; soybean oil 79; toluene 122; water < 0.2. LD_{50} orally in rats: 0.82 g/kg, Deichmann, *Fed. Proc.* 2, 76 (1943).

Sodium salt sesquihydrate, *Dowicide B.* Flakes [prepd according to U.S. pat. 1,991,329 (1935 to Dow)]. Solubility (g/100 g solvent at 25°): acetone 163; denatured alcohol formula 30, 186; ethylene glycol 33; methanol 241; water 113. pH of satd aq soln 11.0-13.0.

Complex with triisobutyl phosphate. $C_{18}H_{30}ClO_3P$, *Trichlorex.* Prepn: Bouillenne-Wallrand *et al.*, Fr. pat. M149 (1961 to Pechiney). Liquid. $bp_{0.01}$ 94-103°.

USE: Fungicide, bactericide.

9456. 2,4,6-Trichlorophenol. Dowicide 2S; Omal. $C_6H_3Cl_3O$; mol wt 197.46. C 36.49%, O 8.10%, H 1.53%, Cl