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Solution of some chemical plant problems associated with the manufacture of insecticides

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SOLUTION OF SOME CHEMICAL PLANT PROBLEMS

ASSOCIATED WITH THE MANUFACTURE OF INSECTICIDES

BY

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A

THESIS

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ILLUSTRATION

SOLUTION OF SOME CHEMICAL PLANT PROBLEMS
# ASSOCIATED WITH THE MANUFACTURE OF INSECTICIDES

1. Introduction

This thesis describes the solutions of a variety of developmental, production, and general engineering problems encountered in a chemical plant. This plant produces resins, solvents, and insecticides. Most of the problems considered here are patented or are of a secret nature. These details are, in the main, satisfactory temperatures, molar ratios, times of reaction, and space-time data. Therefore, it is the purpose of this discussion to be general but, in the main, to give the outline of the thinking which derived these solutions. Some of these solutions were of minor economic value, some were vital to the success of the processes involved. These solutions made a very profitable operation out of the main insecticide involved, a product marketed under the trade name of Chlordane.

The general flow plan of this process is as follows:

1. Production of sodium hypochlorite from sodium hydroxide and chlorine.

2. Preparation of cyclopentadiene.

3. Hexachlorocyclopentadiene production from cyclopentadiene and sodium hypochlorite.

4. Codimerization production from hexachlorocyclopentadiene and additional cyclopentadiene.

5. Final chlorinate production from codimerization product and gaseous chlorine.

A block flow diagram is given in Figure 1.
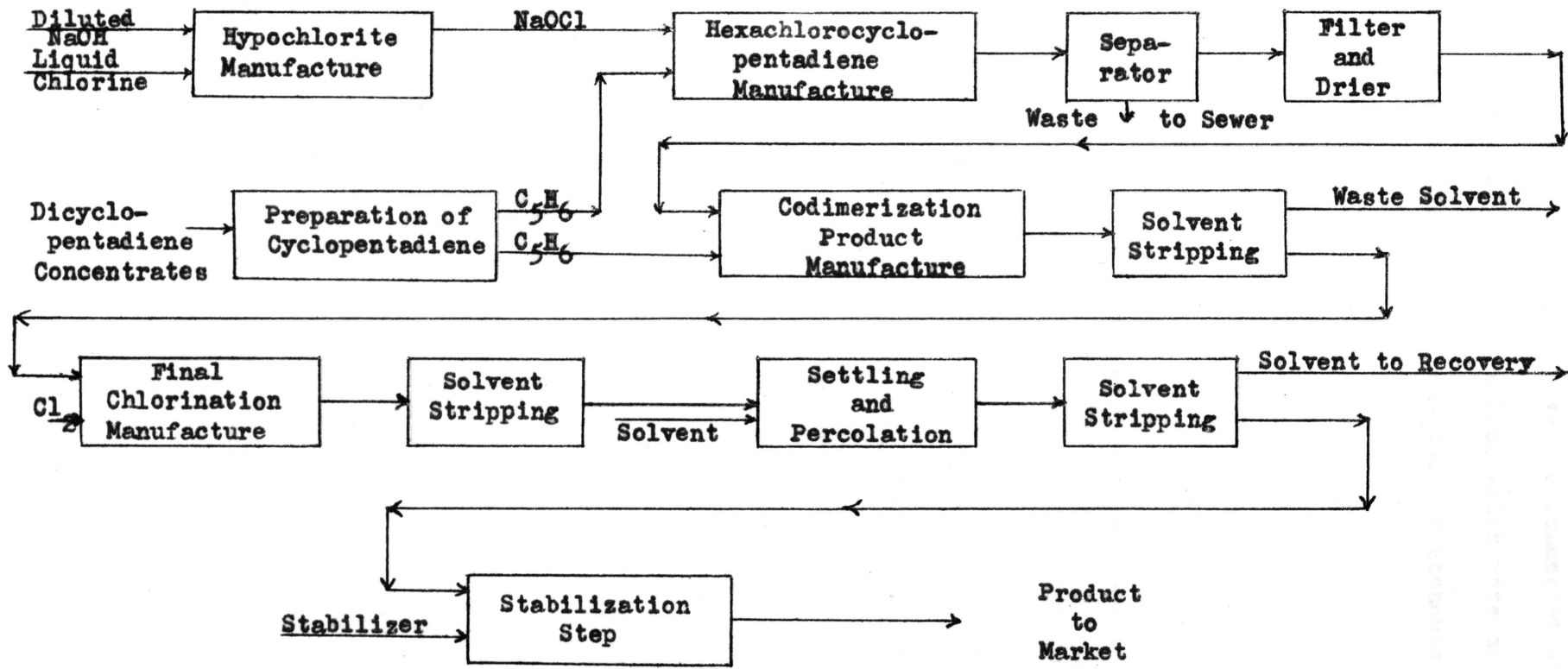
BLOCK FLOW DIAGRAM OF INSECTICIDE PROCESS

Figure 1.

Sections VII to X inclusive are concerned with general engineering problems or with specific problems which were solved. Some of the specific solutions were of considerable economic value at the time.

II. Hypochlorite Reaction and Problems

The reaction required is:

$$2\ NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O.$$
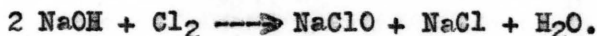
The caustic used was purchased as either 50 per cent NaOH or 73 per cent NaOH and diluted to a proper strength to make the best hypochlorite. Actually, this best strength of caustic was dictated by requirements set in the hexachlorocyclopentadiene reaction. These requirements are discussed in Section III. The equipment was conventional in type. The caustic was pumped into a tank and chlorine introduced through a spider arrangement. Rapid cooling was necessary to keep the hypochlorite stable and to depress a side reaction, which makes sodium chlorate. A maximum of 90° F. is generally considered in the trade as being satisfactory. Low iron content and low sodium chloride content specifications were desirable for the caustic used.

Dissolved or colloidal copper and iron make a very unstable hypochlorite. At one time, a brass impeller in a hypochlorite circulation pump was found to be responsible for the production of unstable hypochlorite. In another instance, some organic contaminants, which had not been removed in the production of the chlorine, were found responsible for unstable hypochlorite. Two carloads of this contaminated chlorine were returned to suppliers.

Enough chlorine was added to the caustic until only a few c.c. of caustic titer remained in a test sample. A completely chlorinated caustic gives a very unstable hypochlorite. Caustic and hypochlorite strengths were checked by the standard volumetric methods.

III. Hexachlorocyclopentadiene Reaction and Problems

The reactants in this case are sodium hypochlorite and cyclopenta-diene. The principal reaction is:

$$6 \ NaOCl + C_5H_6 \longrightarrow 6 \ NaOH + C_5Cl_6$$
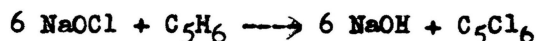
Preparation of hypochlorite is described in Section II. Cyclopentadiene can be prepared from various sources. The raw material source is likely to be coal tar. However, it may also be derived from petroleum sources. Best results are obtained if the source material is a charge very rich in cyclopentadiene. The concentrate as received is mostly dicyclopenta-diene. The properties of these two compounds are given in Whitmore's "Organic Chemistry"[1] and in Karrer's "Organic Chemistry".[2] The boiling point of cyclopentadiene is 41° C. The boiling point of di-cyclopentadiene is 170° C. Trimers and higher polymers of cyclopenta-diene are known. Cyclopentadiene is capable of forming a series of highly colored compounds called fulvenes. Metallic potassium can re-place one hydrogen in cyclopentadiene. This compound is capable of a very wide variety of reactions, generally termed Diels-Alder reactions.

The equilibrium constant for the reaction $2 \ C_5H_6 \rightleftharpoons C_{10}H_{12}$ is of such an order that the reaction proceeds slowly to the right at room temperature and after thirty days is essentially complete.[3] This equilibrium can be reversed and will proceed almost entirely to the left above 700° F. At this high temperature, some higher polymers are formed, but the percentage is very low when a nearly pure dicyclopenta-

(1) Whitmore, F. C., Organic Chemistry, pp. 639-640, 1st. Ed. 5th Print., Jan. 1942.
(2) Karrer, Paul, Organic Chemistry, pp. 603-605, 1938.
(3) Uhrig, Karl, Lynch, Eleanor, and Becker, Harry C., Analytical Chemistry, Vol. 18, No. 9, p. 550, Sept. 1946.

diene charge is used. The final polymer is thought to be $(C_5H_6)_6$.
After rapid dedimerization, the cyclopentadiene is condensed and quickly
fractionated from impurities such as methyl cyclopentadiene, dicyclopen-
tadiene, and dimethylcyclopentadiene. If the overhead cyclopentadiene
is kept below 40° F., little dimerization occurs. Refrigeration is
necessary. If kept as low as 10° F., the stock can be kept indefinitely.
Also, cooling at this low temperature is likely to freeze any water
present in solution.

Fractionation tower residues are polymers of cyclopentadiene.
These residues will react partially with iron rust and often are capable
of spontaneous combustion when exposed to air.

The reaction of cyclopentadiene and sodium hypochlorite can be
carried out in either batch or continuous types of equipment. It was in
this step that serious development work was needed. The principal reac-
tion is given in the first paragraph on Page 5 of this Section. The end
product desired has a maximum content of hexachlorocyclopentadiene. The
reaction in itself is fairly straightforward, but several side reactions
are possible. Each one of the six hydrogen atoms in cyclopentadiene is
progressively replaced by chlorine atoms. It would be expected that the
last two atoms would be the hardest to replace. This is true. Also, the
following reaction is possible in this stage:

$$C_5Cl_6 + C_5H_6 \longrightarrow C_{10}H_6Cl_6$$
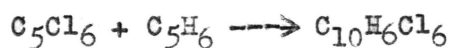
There is no way to prevent some progress of the codimerization reaction
in this step. It so happens that the equilibrium constant for the
chlorination step is much higher than the equilibrium constant for the
codimerization step at the same temperature. Hence, unless excess
cyclopentadiene is added to the mixture, the codimerization reaction is

very inhibited. The search for a proper molar ratio of sodium hypo-
chlorite to cyclopentadiene led to a lengthy investigation, and, at
times, a costly one. It can be stated that the proper ratio is not 6 to
1. The author made a guess on this proper ratio and after several
years' effort, the optimum was still very near the first approximation.
The optimum ratio was about the same in both continuous and batch equip-
ment.

This reaction must be carried out rapidly and the two phases sepa-
rated at once. The cyclopentadiene must be dispersed quickly in tiny
droplets in the hypochlorite phase. This dispersion is relatively easy
and may be accomplished in either batch or continuous process. The heat
of reaction is large, and the temperature must be kept well under con-
trol. If the temperature gets too high, degradation of product by hydro-
lysis is possible; in fact, it has been observed to be nearly complete
when no cooling of a mixture was tried. Cyclopentadiene itself is a
very reactive material because of its special structure. It is a con-
jugated diene, and the two end hydrogen atoms are replaceable by metals
in some cases.[4] Its Diels-Alder reaction with benzaldehyde can be
used as a method of analysis.[5]

As reaction proceeds, the hexachlorocyclopentadiene coalesces in
larger droplets and slowly settles out of the water phase. A proper
maximum reaction temperature was found after considerable experimenta-
tion. This must give maximum yield quickly and yet be carried on at a
low enough temperature that hydrolysis of the product is prevented.
Also, cooling must continue throughout the reactor until the reaction

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(4) Whitmore, op. cit., pp. 639-640.
(5) Uhrig, op. cit., p. 550.

is almost complete. The end product, when left standing at room temperature, will slowly hydrolyze. This hydrolysis reaction is very slow, but at the temperature of boiling water, it is very rapid. Hydrolyzation removes successive chlorine atoms from the five carbon-ring compound.

The effect of solubilized iron or copper on this reaction may be quite pronounced. The impurity may be very small, yet ruin the product. A mixture, which contained enough dissolved iron to make sodium hypochlorite purple, was observed to give a completely hydrolyzed hexachlorocyclopentadiene product at 60° C. Evidently, iron is capable of vastly accelerating the hydrolysis reaction as well as giving other unfavorable side reactions. Iron is capable of chelating hexachlorocyclopentadiene molecules. Also, hexachlorocyclopentadiene can polymerize on heating. The effects of these structural changes do not become apparent until later in the process.

Iron impurities were responsible for production of organic mud. At times, this organic mud comprised over half of the product of this reaction. This mud was an emulsion of hexachlorocyclopentadiene in hypochlorite. Small specks of iron rust or other inorganic impurities were nuclei for this mud formation. When the mud was completely resolved into its components, there were two liquid phases; one was organic, the other was an aqueous phase. Also, there was a very small residue of inorganic solids, insoluble in either phase. Impurities in the caustic as purchased were probably helpful in formation of this mud. The mud can be broken up mostly by heat, but the product is inferior.

Copper is also a catalyst for similar reactions. Chelated compounds are not very suitable for later processing; hence, it is best to prevent these impurities entering from either sodium hypochlorite or

cyclopentadiene charge stocks. It is also wise to keep iron out of
reaction equipment in the hexachlorocyclopentadiene reaction. A clean,
nearly iron-free hypochlorite is essential. When iron is dissolved in
hypochlorite, it may be present in a colloidal form or as a ferrate.
Some sodium hydroxide is always present in the reaction mixture, and
the amount increases constantly until the reaction is complete. Iron
removal from the product will be discussed later.

A search was made for proper construction materials. It would be
expected that glass or glass-lined equipment would be satisfactory for
this reaction. This is quite true. No metal contaminants erode out
of glass equipment. No suitable metal or alloy was found for the main
reaction zone of this part of the process. In the reaction zone, a
Hastelloy C pump impeller lasted two weeks. At the end of that time,
the impeller had almost completely disintegrated. However, at this time,
metal contaminants were quite troublesome and perhaps a ferric chloride
action was responsible for this high corrosion rate. At a later time,
with metal contamination quite low, a Hastelloy C sample in this zone
corroded, but much more slowly. After the main reaction zone is passed,
304 type stainless steel is very satisfactory for transfer pipe. A pipe
of 304 stainless steel lasted several years in this service without
apparent corrosion. At this point, the sturdiness of blue Pfaudler
glass-lined steel should be mentioned. As a settling vessel, a Pfaudler
glass-lined tank was used. Although manufacturers will not claim alka-
line resistance for their product, this settling tank was used for three
years in twenty-four-hour, seven-day week operation at temperatures run-
ning as high as 60° C. The pH of this solution was about fourteen.
Most of the glass was still left on the tank after three years, although

many spots of steel were beginning to show through the glass surface.

After the hexachlorocyclopentadiene reaction is nearly complete, the two-phase mixture flows into the above-mentioned glass-lined settling tank. The size of this tank was quite ample. Actually, some hexachlorocyclopentadiene is so well dispersed that nearly twenty-four hours are necessary for complete settling. However, this well-dispersed product amounts to 1 per cent or 2 per cent of the product, at the most.

Some galvanic action had been noted in reactor transfer piping. A series of checks was made with many alloys. Two strips of dissimilar metals or alloys were placed in hypochlorite solution. Each strip was wired to a galvanometer pole, and readings were made. The largest galvanic current observed was between 304 type stainless steel and malleable iron. Iron was the cathode and stainless steel the anode. All of the 300 and 400 series stainless steels were anodic to malleable iron. Even Hastelloy C was anodic to malleable iron although, in this case, the current was negligible. All dissimilar alloys showed a galvanic current. Negligible currents were observed between very similar alloys such as 309 and 310 stainless steel and between 316 and 317 stainless steel. Only Duriron and Durichlor were cathodic to malleable iron. In pumping hypochlorite, and in handling both charge streams in a most dispersed and active condition, a Durichlor pump was undamaged after three years' service. A Hastelloy C impeller lasted two weeks under the same conditions.

A clean-up of dissolved iron in the hexachlorocyclopentadiene product was accomplished with a unique filter. The organic phase was separated in a settler and pumped through this filter to intermediate storage.

It had been observed in the laboratory that fine filter paper cleaned up hexachlorocyclopentadiene in a manner satisfactory for later processing. It was deduced by the writer that the filter paper was adsorbing ferric chloride and water. The paper was also filtering out fine solids and bits of organic mud. This observation was later the basis for the construction of a plant filter using cellulose. As suggested before, just how dissolved iron could be present in alkaline hypochlorite is difficult to see, since ferric hydroxide is so very insoluble. Perhaps the iron is present in the hypochlorite in colloidal form. It is known that some organic compounds such as benzene are excellent solvents for iron compounds.[6] Processes are known in which an organic solvent can be used for the extraction of ferric chloride from an aqueous solution. Distribution ratios as high as 6,000 to 1 have been noted for such an extraction.

The product hexachlorocyclopentadiene is a very remarkable and versatile solvent. By laboratory test, it was proved capable of dissolving iron salts.

Chloride ion is present in the hypochlorite phase in abundance. Also, hydrolyzed hexachlorocyclopentadiene would produce chloride ions. Ferric chloride was proved to have been removed by cellulose.

The cellulose also adsorbed considerable water. The water adsorbed had been in true solution, as adsorption took place both under pressure and under vacuum conditions. As a drying agent, it equalled the drying powers of anhydrous sodium sulphate and exceeded that of Johns-Manville Super Cel. Removal of this water is probably as important as the

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(6) Groggins, P. H., Unit Processes in Organic Synthesis, 4th Edition, p. 213, 1951.

removal of ferric chloride. Dissolved water will certainly hydrolyze hexachlorocyclopentadiene in the next reaction under the reaction conditions when a trace of iron is present. With no iron present, little hydrolysis occurs. The amount of water removed may run as high as 1 per cent by weight of the product dried.

The dried product could be checked for effectiveness of the clean-up step by putting a test tube of hexachlorocyclopentadiene in boiling water for five minutes. If the clean-up was good enough for later processing, the sample would be very slightly deepened in color. If the clean-up was not adequate, the sample would be very black. This test was used to demonstrate that no other drying agent except cellulose was adequate, because no other drying agent removed iron impurities to a low enough level. This was proven true by chemical analysis.

It would be difficult to overestimate the value of this cellulose filter, or drier, in the manufacture of the final product. Only when the filter was installed and functioning properly was a light-colored end product possible. Only when a light, amber-colored hexachlorocyclopentadiene was produced could a light-colored finished product be made. Undesirable impurities in the final product had been running as high as 40 per cent before installation of the first crude cellulose filter. These losses dropped at once to 6 per cent and to less than 1 per cent when development was complete.

Recovery of hexachlorocyclopentadiene from the waste hypochlorite solution was attempted, but no commercial method of recovery was found. It was observed that both cellulose and Hy-Flo Super Cel were effective but not practical. The organic material in the aqueous phase was present as a dispersion of oil in water.

IV. Codimerization Reaction and Problems

The principal reaction is:

$$C_5Cl_6 + C_5H_6 \longrightarrow C_{10}H_6Cl_6$$
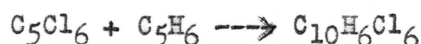
Lower chlorinates than C_5Cl_6 also react in the same manner. Some of these lower chlorinates were always present in manufactured hexachloro-cyclopentadiene. The exact quantities used in plant practice only approximated equimolar quantities.

Careful laboratory analysis determined practical amounts of cyclo-pentadiene to add to a batch of hexachlorocyclopentadiene. The purity of cyclopentadiene to be used was tested as described on Page 7. Nearly pure hexachlorocyclopentadiene has the following properties, as adver-tised by Hooker Electrochemical Company:

Molecular weight	272.79
Freezing point	-2°C.
Boiling point	236°C.
Distillation range (A.S.T.M.).	$236-245^{\circ}$C.
Refractive Index n 20°/D	1.564
Specific gravity $15.5^{\circ}/15.5^{\circ}$C.	1.715

They also say: "As a highly reactive intermediate, it enters readily into many different types of reactions. Some of the end products are acids, acid chlorides, acid anhydrides, esters, amides, ketones, dike-tones, quinones, acetals, nitriles, and fluorocarbons. The probable fields for this new chemical are: insecticides, dyes, pharmaceuticals, resins, germicides, and fungicides. Hexachlorocyclopentadiene is a yel-low to amber-colored liquid with a pungent odor". Characteristically its reactions would be expected to be of the Diels-Alder type. It has

a positive heat of formation. It has a very small heat of combustion. The impure material as produced burns slowly with a very smoky flame when a natural gas-oxygen torch is held on the liquid surface. This flame extinguishes at once when the torch is removed.

Cyclopentadiene is also capable of most of the reactions mentioned as possible for hexachlorocyclopentadiene. As mentioned previously, cyclopentadiene is capable of polymerization up to $(C_5H_6)_6$ at least. Hexachloropentadiene is capable of similar polymerization except that the point where the polymer is a black, insoluble solid is probably reached at a polymerization number of less than six. Cyclopentadiene can also be chelated with iron, as shown before.

The kinetics of the reaction $C_5Cl_6 + C_5H_6 \longrightarrow C_{10}H_6Cl_6$ were studied carefully in pilot plant work. A cursory examination of the reaction equation may lead one to expect a second order reaction, but often, apparent second order reactions are first order reactions when the kinetics are studied carefully. The reaction speed for any given temperature is evidently much less than for the previous reaction of cyclopentadiene with hypochlorite. Actually by using twice the required cyclopentadiene to react with hypochlorite, the double reaction can be completed at once, but the product is inferior as regards density and chlorine content. Products of low density and chlorine content are too liquid. The pure $C_{10}H_6Cl_6$ is a snow-white, crystalline solid. By taking careful pyncnometer determinations of various laboratory and pilot plant codimerization reaction products and plotting results, an apparent gravity of pure $C_{10}H_6Cl_6$ of 1.6000 was obtained by the author. This is nearly correct. The pure product exhibits a regular crystal habit, making a crystal of twenty-two

faces. This can be obtained by repeated crystallizations from carbon tetrachloride.

Both reactants in this case are liquids as charged. The plant product is a sugary solid when cool. In some cases, it was very solid when cool; however, at the temperature of reaction, crystals are evident, but the mixture exhibits properties like a viscous liquid. The reaction will proceed over a considerable range of temperature, although an optimum was found where reaction was rapid and complete, and side reactions were still fairly inhibited. Probably the most important competing side reaction was the dimerization of cyclopentadiene. The K of this reaction is much lower than the K of the codimerization reaction at the optimum reaction temperature.

The reaction is very exothermic as the double bonds are reduced in number. $C_{10}H_6Cl_6$ has only two double bonds remaining. The dimerization of cyclopentadiene is also very exothermic but, as mentioned, the reaction K is so much lower, that the apparent end of the reaction can be easily observed. An overall heat transfer coefficient U of 20 B.T.U./(hr.)(sq. ft.) (F^o.) was observed in this reaction in glass-lined equipment. The product at this stage must have excess cyclopentadiene and dicyclopentadiene stripped out by high vacuum and it is then ready for the next production step.

In early work with the codimerization reaction, an organic solvent had been used in the hexachlorocyclopentadiene reaction to carry the cyclopentadiene, and this solvent remained until the codimerization reaction was complete. It was thought at that time that a solvent assisted in the phase distribution of the reactants. This solvent was usually benzene. At that time, the codimerization reaction was carried

out at a lower temperature and required a much longer reaction period.
Actually, the reaction kinetics were very different when a carrying sol-
vent was used in the codimerization reaction. During the period in
which a solvent was used, the author constructed and operated a small
pilot plant stripper to remove the benzene from the finished codimer-
ization product. Then, a few months later, the author designed a plant
stripper made of 304 type stainless steel of 11 guage thickness. This
is described here because progress at a later time made it unnecessary
to use this stripper. At the time of its construction, commercial pro-
duction was made possible by its use. The stripper was three feet in
diameter and four feet long in its straight cylindrical section. A 45°
cone at the bottom lowered the diameter to twelve inches. Another
cylindrical section fifteen inches long comprised the bottom section. A
$1^{1}/2"$ pipe, extending downward about twenty feet to a reservoir tank,
drained the bottom of the stripper. The bottom cylindrical section was
enclosed in a steam jacket. Heated product with solvent was pumped into
the stripper a few inches from the top. A four inch vacuum outlet from
the top of the three foot diameter section led downward to a Nash vacuum
pump suction inlet. Alternate disk trays, followed by doughnut trays,
were in the three foot diameter section. This gave good distribution of
the viscous and partially solid product so that benzene could be boiled
out. Whenever the best product was made, the downpipe tended to plug,
but mostly it was operable and served its purpose.

The author designed and operated a small continuous reactor and
stripper for kinetic studies of this reaction. Continuous reaction was
feasible. However, this continuous reaction was carried out using only
the reactants. These stripping operations were carried out at about the

optimum temperature, which was later used as a reaction temperature.

The codimerization product is probably capable of iron chelation, although not as easily as is hexachlorocyclopentadiene. The product can be handled successfully at a much higher temperature than can the previous hexachlorocyclopentadiene product. As iron contamination is lowered, the reaction temperature can be raised. Also, excess cyclopentadiene must be removed as soon as the reaction ends.

As this reaction is completed in plant process and stripping off of excess cyclopentadiene has been completed, the product is very crystalline in nature. Agitation is now difficult and more labored. In the plant process, the next step must be started immediately. If allowed to cool to room temperature, the product might set up solid.

V. Final Chlorination Reaction and Problems

The principal reaction is:

$$C_{10}H_6Cl_6 + Cl_2 \longrightarrow C_{10}H_6Cl_8$$
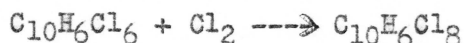
The $C_{10}H_6Cl_8$ is an advertised insecticide. The final step is quite sim-
ple. The use of chlorine makes glass-lined equipment almost mandatory.
The reaction does not proceed entirely as the equation would suggest.
The charged $C_{10}H_6Cl_6$ is not pure. As produced, it is so nearly solid
that it is difficult to handle. Some chlorine should be introduced into
the reaction kettle as soon as vacuum stripping of excess solvent from
the codimerization product has been completed. As soon as some chlorine
has reacted, the mass becomes much less viscous and can easily be agi-
tated. The solution becomes more and more fluid as chlorination pro-
ceeds.

In this case, side reactions are to be expected and are desirable.
As suggested by Groggins[7], the maximum reaction of chlorine into a
double bond would occur when the temperature is fairly low and the sub-
stitution chlorination would occur in a larger degree at higher tempera-
tures. This is partially true. In this case, both reactions are desir-
able. The double bond in the five-membered ring portion of the charge
$C_{10}H_6Cl_6$ should fill easily, and it does. The filling of this double
bond is the dominant reaction, although considerable substitution also
occurs. Substitution is made evident by evolution of by-product hydro-
gen chloride. The reaction is highly exothermic. The end of the reac-
tion can be observed easily when the large heat evolution diminishes
suddenly and free chlorine appears in the waste gases in large quantities.

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(7) Groggins, op. cit., p. 213.

When it is pure, the final product of this reaction is a white viscous liquid, although some crystals are likely to be present at room temperature. The plant product is an amber viscous liquid having a viscosity at room temperature similar to that of molasses. The pure product has a melting point near 0° C. This is not a definite melting point but rather a transition point, or softening point.

The method of the final reaction has been described as it was on completion of development. It was thought by some of my colleagues that chlorination with gaseous chlorine, through a layer of crystalline material five to six feet deep, would be impractical if not impossible. The chlorination without solvent was suggested by the author. Development in the laboratory and plant was carried out under his direction. Codimerization and final chlorination reactions had to be carried through without any interim cooling allowed. The respective products were tested carefully and found to be equal to or better than standards of quality required. The final product color and viscosity were better than products made in the plant previously. Other tests required were also satisfactory. The very definite end points of both reactions were observed carefully. When transferred to plant practice, the reaction was much easier to handle than when carbon tetrachloride had been used as a solvent. Cooling of the batch in a glass-lined kettle was more difficult, but almost as much chlorine could be added per hour as before, and the batch could contain three times as much product. The very first batch produced a better final product than had been made in the plant at any previous time.

Up to this time, all plant final chlorinations had been made in carbon tetrachloride as solvent. Reactions without solvent carriers

were very slow to be accepted. For about three years, the amount of
chlorine was carefully metered to approximate the stoichiometric amount
required by the idealized equation. When demands were made for a higher
viscosity product, a newer method was tried. This method was developed
in the laboratory and then put into practice. Chlorine was added to the
mixture until the heat of reaction diminished to a low point and much
excess chlorine was given off. The product was a satisfactory one in
every way. It was a much more stable product than that previously pro-
duced. The previous plant product darkened much more in long term stor-
age. Also, the new product was a heavier material. Yields were raised
as much as 40-50 per cent. Undoubtedly, chlorine was filling the free
double bond in the codimerization product as well as substituting in
place of at least one hydrogen atom. A close study of waste gases,
given off throughout the whole term of the reaction, showed that the
end point was quite definite.

A sudden increase of 40-50 per cent in production was pleasing to
the management. A breakdown of vacuum equipment for stripping carbon
tetrachloride and excess chlorine occurred at the same time. The last
vacuum pump on hand was inoperable, and no more were on order. The
author then designed a home-made steam jet, put it into operation, and
increased production still more. This steam jet vacuum equipment was
more satisfactory than the previous vacuum pumps used. The equipment
will be discussed later.

The goal of the entire development project was to make a light,
amber-colored product having other desirable properties such as a small
density variation, a small per cent chlorine range, proper viscosity,
and a desirable insecticidal activity. The most important steps in

attaining these goals were: a satisfactory hexachlorocyclopentadiene reaction, and the very important clean-up of this product.

After completion of chlorination batches with a solvent present, carbon tetrachloride had to be stripped out under high vacuum. When no solvent was used in chlorination, stripping under vacuum was still necessary. This stripping process removed dissolved chlorine and other volatiles.

At this stage, the product was a viscous liquid when cold. On a commercial basis, it was always necessary to attempt some purification step for this final product. At this point, the liquid product was dissolved in an aliphatic hydrocarbon. Most of the unwanted impurities were insoluble in this solvent. In early development and production stages, a sulfuric acid treatment removed the insolubles and other impurities. These insolubles were always very rich in iron content. The insecticidal activity of this waste product was often higher than the desired commercial product, but a use of this waste product as an insecticide was impractical because of its insolubility. This sulfuric acid treatment was always wasteful, but progress in development produced better methods. At times, losses had been as high as 50 per cent in this step. When an adequate hexachlorocyclopentadiene filter was used, the final clean-up became simple and easy. This consisted of a percolation apparatus containing two adsorbents. One adsorbent removed iron chelates and the other removed various unstable underchlorinates.

After percolation, or acid treatment, the product was charged to a continuous stripper, which had been partially designed by the author. The stripping vessel was made of copper. Essentially all solvent was stripped out under high vacuum, with vacuum provided by a TS-12 Nash

Hytor Pump. Hydrocarbon solvent and water composed the effluent stream from the pump. A simple phase separation removed all but a trace of water from the recovered solvent.

This final step gave little trouble in the matter of selection of proper metals or alloys. Either stainless steel or copper would have been suitable as a stripper construction material, whereas copper would have been unsuitable in any previous step.

After stripping out the solvent used for purification, the final product was pumped into a glass-lined tank and mixed with a small quantity of stabilizer. The product tended to slowly darken on standing and give off hydrogen chloride, if not stabilized. Hydrolyzation of this product could occur in air very slowly. A high residual action is desirable in this insecticide, hence it must be stabilized. It was learned that stabilization must be done within a few hours, if some darkening of the product was to be prevented. Product made, when carbon tetrachloride had been used as chlorination solvent, exhibited this characteristic quite markedly. When amber-colored final product was made, its stability was quite high, but a stabilizer was mixed in the product at once as a precaution.

After testing the product for insecticidal activity, it was ready for sale.

VI. Various Equipment Innovations

All of the equipment innovations to be mentioned here were designed by the author. The first one to be discussed is a chlorination waste gas scrubber. For two years, waste hydrogen chloride and chlorine were piped off into the field about one hundred fifty yards distant and vented into the air. This was never satisfactory. Two carefully engineered waste gas scrubbers were purchased at different times from different manufacturers. One tower blew up, the other plugged up, and the tile pipe was cracked when pressure developed. These accidents were due to the fact that chlorination was a batchwise operation giving off waste gases in a widely variant fashion. At first, no gas was emitted, because all chlorine was being absorbed. Later, the amount of gas increased slowly until, at the end, large volumes of free chlorine were given off. Most of the waste gas was hydrogen chloride, which could be neutralized by sodium hydroxide. At the end of the chlorination reaction, the waste gas was nearly 100 per cent chlorine and required twice as much caustic for neutralization. Also, at all times, the temperature of reaction was high enough that small portions of underchlorinated cyclopentadiene products were entrained in waste gases. The quantities entrained were only enough to be troublesome and slowly plug any waste gas pipes used.

When the gases were vented into the air, they were quite troublesome to plant operators, when the wind was in the wrong direction. When the atmospheric conditions were foggy, the gases were kept in the plant area much too long before dispersion. On one occasion, it was necessary to pay for a farmer's soybean crop.

Now, at the same time, an alkaline waste was continuously running to the sewer from the hexachlorocyclopentadiene reaction. Early in developmental operations, this waste hypochlorite solution, having a pH of about fourteen and having sodium hydroxide and sodium chloride dissolved in nearly equal molal proportions, was recycled. The solution was once again batch chlorinated. After another cycle in the hexachlorocyclopentadiene reaction, the waste hypochlorite, now having a doubled amount of sodium chloride present, was sewered. When a truly continuous hexachlorocyclopentadiene reaction was provided, all waste hypochlorite solution was sewered without any recycling. With a small change in the sewer line, this waste solution flowed into one side of a thirteen hundred gallon concrete sump. All waste chlorination gases were led into the middle of the sump with a cast iron line. The last section of pipe was glass pipe. This was immersed in the sump liquid about six inches. All liquid drained continuously to the main sewer from another side of the sump. This permanently took care of the disposal problem, as the waste alkali always exceeded the waste gases in molar quantities necessary for neutralization. Needless to say, this one step improved employee morale. It was also beneficial in lowering the total alkalinity of water effluent from the plant pond.

At one time in the development of the hexachlorocyclopentadiene reaction step, the final mixing of aqueous phase and organic phase was accomplished by pumping the mixture through a series of globe valves. The fact that this adequately mixed the reactants was discovered by accident. However, this equipment was retained as an integral part of the reaction system for several years. It was found that the reaction could be speeded up by the proper setting of these valves. After proper

dispersion of the organic phase, the reaction went quickly to completion
at the maintained temperature. This method of mixing was later abandoned
as progress was made; and, as production rose, proper dispersion was
made at an earlier stage. Actually, this globe valve mixing operation
reoriented thinking in this operation. This operation demonstrated that
a good product could be made at a higher temperature in much less reac-
tion time than was formerly thought possible. It also demonstrated, to
some extent, the level of mixing necessary for this operation. The
power input necessary was much less than that thought to be required.

For a considerable portion of the time in which carbon tetra-
chloride was used as a solvent in chlorination work, a solvent recovery
and drying system was used. In itself, it was very simple. Equipment
used was designed by the author. Many people dislike to use recover-
ed chloroform and carbon tetrachloride solvents. The carbon tetra-
chloride to be recovered was stripped out of final product batches by
a high vacuum process. The condensed carbon tetrachloride had, as
impurities, a little chlorine, hydrogen chloride, and some entrained
organic chlorinates. All of these impurities were present in very
small percentages. This condensed carbon tetrachloride was pumped
into a caustic wash tank as quickly as possible. One volume of one
per cent sodium hydroxide was mixed with two volumes of carbon tetra-
chloride by continuous circulation with a centrifugal pump. This simple
mixing operation adequately neutralized the acid impurities. A caustic
wash was followed by two water washes, and sufficient time was allowed
for phase separation. Then, the carbon tetrachloride phase was slowly
percolated through a column of silica gel six feet high and twelve inches
in diameter. The silica gel, as charged, was about 14-20 mesh non-

catalytic gel produced by the Davison Company. Percolation rates varied from 0.1 to 0.5 feet per second. When fresh gel is used, the carbon tetrachloride can be dried rather rapidly. Rate of drying should be slow, as resistance through the bed increases with water adsorption. The silica gel used is capable of drying some hydrocarbons to a water content of 10 p.p.m., as given in Mantell.[8] The recovered carbon tetrachloride was much drier and freer of impurities than newly purchased carbon tetrachloride. When the drier was properly operated, a very good recovered chlorination solvent was produced. Silica gel adsorbs carbon tetrachloride at first, until saturated. Then, water slowly displaces the carbon tetrachloride. Small amounts of impurities, more polar than carbon tetrachloride, are adsorbed and remain adsorbed.

It is easy to determine when the gel is exhausted by putting a small section of glass pipe in the outlet stream and filling this section with cobaltous chloride impregnated silica gel. This indicator gel turns pink when saturated with water. It retains its normal blue color until the gel above it is saturated, and water is adsorbed by the indicating gel. It should be noted that this silica gel can be dried at 250° C. for twelve hours and reused. The process of drying liquids gradually cracks the gel into smaller and smaller pieces until it is too fine for liquid drying. It was found in practice that new gel could be dried and reused twice, thus making it possible to use the gel three times before it became too fine for reuse. A discussion of uses of silica gel in liquid drying is given in Mantell[8] and Perry.[9]

Another piece of equipment, which was important for some time, was

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(8) Mantell, C. L., Adsorption, 2nd Ed., pp. 173-184.
(9) Perry, J. H. Chemical Engineers' Handbook, 3rd Ed., p. 914.

a caustic scrubber used for neutralization of acid gases and carbon tetrachloride stripped from the final chlorinated product. During a twelve-month period, $12,000 worth of vacuum pumps had been ruined in this operation. Under vacuum, the carbon tetrachloride was boiled off and condensed with a cascade type glass coil condenser. This condenser was observed to give an overall transfer coefficient U of 125 B. T. U./(hr.)(sq. ft.)($F.^{\circ}$), which is very good for a glass exchanger. The condensed carbon tetrachloride then drained into a receiving kettle. When the kettle became full, carbon tetrachloride was pumped out to the solvent recovery system. Non-condensable gases and some carbon tetrachloride were pulled on through the receiving kettle by a vacuum pump.

A crisis arose when all vacuum pumps on hand had been corroded until inoperable, and no replacements could be received for several months. It was necessary to improvise quickly. A shop-made steam vacuum jet was constructed. This was in operation within twenty-four hours after its design was completed. It was made from all standard fittings. Only one weld was necessary. Supply steam was carried in a one-inch line. The suction end was a two-inch section. The line was then swedged down at approximately a twelve degree angle. The Venturi section was four inches long, diverging at the same angle into a two-inch tail pipe. The steam supply was reduced to one-fourth-inch pipe, ending a fraction of an inch from the entry into the Venturi section. This jet had to be repaired after each batch, but usually only one fitting had to be replaced. Materials of the jet were wrought iron or malleable iron.

Steam supply pressure was one hundred fifty p.s.i.g. Exhaust pressure was atmospheric. This steam jet gave the vacuum necessary to distill off carbon tetrachloride and dissolved waste gases from a one thousand

gallon chlorinator. Most of the carbon tetrachloride was distilled off at ten to fifteen inches Hg. of vacuum. Then, residual carbon tetrachloride was slowly removed down to a point as low as the jet or vacuum pump would provide. This shop-made steam jet gave a vacuum of twenty-two inches of mercury. The cost of this equipment was low, and production was maintained, even being raised 20 per cent. Later, an effective steam jet, built out of materials which would resist hydrogen chloride, chlorine, and carbon tetrachloride, was purchased, tested, and put into operation. Naturally, the management was quite pleased that production could be maintained and raised under these conditions.

VII. Steam and Water Needs

After the development work on the above-described insecticide process was completed, various steam and water surveys were made for the entire chemical plant. Each water usage was determined carefully, and many excessive amounts were noted. A study of proper water usages required several months. If the water could be returned to hot wells, it was returned. A few unnecessary uses were eliminated. Each exchanger need was assessed, and the reason for excessive use or improper operation was sought. In some cases, overall transfer coefficients were obtained. If they were too low, means were often found to improve them.

It was found that a cooling tower basin had been spilling over its curb intermittently for a period of several years. The reason for this spillage was that one cold well pump was pulling suction from two separate tower basins, one being four feet away, the other being twenty feet away. Naturally, the pump received more water from the nearest basin. Also, the curb of the basin twenty feet away was several inches lower than the curb of the nearer basin. Raising the curb of the farthest basin eighteen inches corrected both faults. This was important merely in tidying up simple engineering details, many of which cost the company considerable expense.

The plant water supply had been obtained from two different sources; one supply was from the nearby city, the other from two plant wells. The main source of supply had been the city water. Plant well water had been used when the plant was quite small. Also, a plant cooling pond had been used in earlier days and was still in use as a reservoir. Water, which had not been warmed up as high as 20° C., was piped

to this reservoir and brought into the cooling tower system gradually. The system had "grown like Topsy". Each route had to be checked carefully and accounted for. This whole system was revised considerably. The plant wells were cut out of service soon. For one thing, their solids content differed from the water furnished by the city. This complicated water treating, as the water treatment had to be based on a water whose composition was constant. With the plant wells in use, this was impossible. The composition of the water from the city source was fairly constant. The composition of plant well waters varied continually. City water composition was as follows:

Ion	Equivalents per million
$HC\bar{O}_3$	4.85
Cl^-	0.222
SO_4^{--}	0.162
Free CO_2	0.721
Ca^{++}	4.28
Mg^{++}	2.53
$Ca^{++} + Mg^{++}$ Hardness	6.81
Alkalinity	4.93
Non-Carbonate Hardness	1.88

Treated water composition was as follows:

Ion	Equivalents per million
CO_3^{--}	1.00
Cl^-	0.23
SO_4^{--}	0.60
OH^-	0.17
Ca^{++}	1.00

Ion	Equivalents per million
Mg^{++}	0.30

Ground waters of the area contained mostly bicarbonate hardness. This condition is quite common in glaciated areas of the northern states. The city water was derived from two large but shallow wells. Plant well water washed through similar underground formations, but these plant wells were not pumped continuously. Approximate total alkalinity of the city water, expressed as p.p.m. calcium carbonate, was five hundred. All treated water used in cooling tower circuits was treated in an Infilco Accelator apparatus. Rated capacity was one hundred fifty gallons per minute. Lime was used as a precipitant. Enough sodium aluminate was added to help flocculation. Operation of this type of treating unit is described in Perry's Chemical Engineers' Handbook.[10] Softening action takes place in a sludge blanket. This type of treatment precipitates carbonate and bicarbonate ions as well as some of the magnesium. The pH of treated water was 10.2. This treatment reduced total solids by about 60 per cent. Accelator effluent water was fed into cooling tower basins automatically as required to maintain proper levels. Considerable water usage, in excess of cooling tower needs, was pumped constantly to units demanding cold water. Most of the needs in the insecticide unit were for this fresh, cold water, the temperature of which was never warmer than 68° F. Much of this cold water, when used, cycled into a cooling tower basin. If this water was in excess of need, it could be reservoired or sewered as required.

The plant cooling tower circulation included four cooling towers.

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(10) Perry, J. H., Chemical Engineers' Handbook, 3rd Ed., p. 947.

Two were of the atmospheric type, and two were forced draft cooling towers. The total possible duty of these towers could be as high as 15,000,000 B. T. U./hr. California Redwood was used in the construction of these towers. This is a very long-lived wood commonly used in cooling towers. It will last many years unless pH of the water rises too high, leaching away part of the wood structure, or it can be deteriorated by other water or fungi maladjustments.

A careful study of conditions existing in each of the four plant cooling tower basins demonstrated that pH values were too high for optimum conditions.[11] Total dissolved solids were not as high as allowable. Hence, enough tower water was lost in circulation to keep total solids low enough. Cooling tower water is concentrated by evaporation of water, which cools the circulated water. This water can gradually increase in pH, because of absorption of CO_2 from the air. This increase in pH is very slow, so very little sulphuric acid is necessary to control this condition. Acid is necessary because the Langelier calcium carbonate saturation index is too high.[11] Often, chrome salts or some similar materials are added to cooling tower basins as needed. Accumulation of algae must be prevented also. Algae can reduce best distribution of water being pumped into the top of each tower.

Until the time that this survey of water and steam usages was made, boiler feed water had been supplied from the effluent of sodium zeolite treaters. Fresh city untreated water was charged to these zeolite treaters. There had been numerous complaints of the high boiler blow-down usages. These blow-down usages were found to be as high as

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(11) Data Book, The Permutit Company, p.52, 1944 Ed.

5 per cent of the total boiler charge. Solids in the boilers had been kept fluid by addition of a small amount of disodium phosphate in the feed water system. This treating method was satisfactory except for an excessive use of salt used to reactivate the zeolite treaters and an excessive loss of steam in blow-down. Zeolite treatment only exchanged sodium ions for calcium and magnesium ions, not appreciably reducing total solids; in fact, the treatment may increase total solids a little. After data was gathered, the writer was instrumental in persuading the management to use Accelator treated water as charge stock to the zeolite treaters. When in operation, this change in charge water lowered blow-down losses nearly 60 per cent.

In this chemical plant, very little condensate was returned to the boilers. Corrosion always was observed in steam and condensate lines. Water charged as boiler feed water was preheated, but no oxygen removal was undertaken. Steam condensate line corrosion was due, in this case, not to oxygen alone but to a combination of oxygen and carbon dioxide. If oxygen is removed, carbon dioxide is not capable of corrosion alone. This condition was pointed out to the management. On one cold morning, one hundred thirty-three steam leaks of various sizes were observed in the plant area. Some were fairly large. These were nearly all due to steam condensate corrosion. When the boiler feed water was lime treated and zeolite treated, most of the carbon dioxide, which had formerly been produced with steam, was kept out of the system, and much less corrosion was observed.

A survey was also made of all steam usages; unnecessary wastages, and excessive usages were pointed out and many savings effected. All usages were estimated and checked occasionally to see whether any sav-

ings were being made, the findings being reported to the operating foremen.

No type of steam trap used seemed very effective against the constant corrosive attack of both CO_2 and oxygen in the steam before the change in water treating was made. After a short time, the trap would plug with rust and be inoperative. This accounted for much waste.

After the survey of steam and water needs was completed, water, steam, condensate, and sewer lines were plotted on a large plant map.

Insulation needs were checked and recommendations made. Some outdoor steam insulation was in very bad condition. Several steam lines had outdoor insulation which was not weatherproofed. When this insulation became wet from either rain or snow, heat losses could be worse than those losses realized when no insulation was used. The main steam headers were in general well insulated. Most improvements were made in smaller lines. Some lines were reorganized.

VIII. Preparation of Cyclopentadiene Charge

At one stage of operations in this plant, it became likely that a charge stock source might be cut off and that operations in one department might cease unless an alternative charge stock could be obtained. The research department had analyzed a possible charge stock, which contained the necessary cyclopentadiene. The amount present ranged from 5 per cent to 10 per cent. Charge stock analyzed was used for making resins normally, but since it was plentiful, the research department suggested a means of recovering the cyclopentadiene content for the manufacture of insecticide. The writer assisted in small-scale work-up of these operations. Problems, in this stage, were solved easily. When plans were made for the commercial plant, it was thought that when a controlled dimerization of cyclopentadiene was attempted, high pressure equipment might be necessary. It was generally thought, by the management, that pressures might rise as high as those used in handling liquid propane. Some literature sources had stated that cyclopentadiene is capable, in some cases, of spontaneous decomposition and very violent explosions. The reaction described is, in some ways, similar to acetylene decomposition and explosion. The writer questioned whether this should or could occur, unless very high pressures were built up. This supposition seemed confirmed by a careful search of literature covering most of what is known of the reactions of cyclopentadiene. It was suggested, by the writer, that if enough free head space were left in the vessel, the reaction should not develop a pressure higher than fifty p.s.i.g. at 210° F. A small test batch was set up and tested at 210° F. The pressure actually developed was fifty-three p.s.i.g.

A plant recovery system for this important raw material was built

up and was in operation in a few weeks time. There were very few diffi-
culties, which developed in the operational procedure. As a result, the
impending loss of business was averted and production of the finished
insecticide was completed as per schedule.

IX. Clean-up of Resin Solutions, Drying of Charges

On one occasion, a resin solution, produced in this plant, pre-
sented a clean-up problem. Sales were seriously threatened unless the
problem could be solved. As produced, the resin was too unstable at the
temperature necessary when mixed in varnish cooks. It was suggested by
the author that this difficulty might be due to the presence of iron
contaminants. Cyclopentadiene and methyl cyclopentadiene are capable of
slight iron reaction. It was also suggested that some form of cellulose
might be useful in adsorption of this iron in a simple filtration. The
idea worked in practice, a clean-up operation was put into service, and
a satisfactory solution of the problem was obtained.

On another occasion, a plant problem arose in the manufacture of
another resin in solution. In this process, the chemical boron tri-
fluoride was used as a catalyst to promote resin formation. It had been
observed many times in laboratory work that maximum yields were obtained
when this reaction was carried out at very low temperatures. Some col-
leagues thought that best yields were obtained at -40° C. to -80° C.
This problem had been of concern to the research people for some time.
The idea that best yields could be obtained at very low temperatures was
so well accepted that, at one time, purchase of refrigeration equipment
worth $250,000 was considered.

The author was asked to determine a series of moisture contents
in some of the resin charge solutions before boron triflouride was
added. Karl Fischer reagent was used to make the analyses. The me-
thod used for plant drying of these resin charge solutions will not be
described, but the method is generally considered adequate for most such

purposes. However, analyses showed that the driers removed moisture only to an equilibrium percentage of water at a given temperature. Differences in these equilibrium percentages would be considerable in summer as compared to winter. After these water contents had been obtained for several charges and several temperatures, it was suggested by the author that these equilibrium water contents might have something to do with lower yields at higher temperatures. It was suggested that equilibrium moisture contents must be very low at the low temperatures considered. Figures from the Karl Fischer determinations suggested that this equilibrium moisture left in the resin solutions was capable of reacting with as much as 40 per cent to 50 per cent of the boron trifluoride catalyst added. Any moisture present in such a quantity certainly would reduce yields by making the boron trifluoride ineffective. These ideas were presented to the management.

The drying of hexachlorocyclopentadiene, as described in Section IV, was eventually done with a cellulose drier. The possibility of determining the moisture present, with a Karl Fischer reagent was considered. However, on close examination, it was thought that hexachlorocyclopentadiene was capable of reacting with all of the reagents used in making up the Karl Fischer mixture. Obviously, this test was impractical. A trial was made to see if the hexachlorocyclopentadiene manufactured in the plant could be dried by distillation. This proved to be very impractical because up to about 210° F., a very small percentage of the material distilled over. About 99 per cent of the material remained behind as tars and carbon. Large volumes of hydrogen chloride gas were evolved. This rather complete destruction of hexachlorocyclopentadiene was apparently caused by 1 per cent water present

plus a much smaller percentage of iron salts. The same material could take the same treatment for one-half hour after complete drying, without damage. Hexachlorocyclopentadiene would gradually polymerize if held at 210° F. for twenty-four hours, even when dry. However, reaction times required were not of this order.

The water present was finally estimated by drying with sodium sulphate and with cellulose. It was possible to estimate approximately the amount of water that sodium sulphate was capable of absorbing. Cellulose was approximately equivalent to sodium sulphate, pound for pound, in its capacity for removal of water from the solution. Hexachlorocyclopentadiene samples, one of which was dried with sodium sulphate and the other with cellulose, were compared in a Lumetron instrument. In color and clarity, the samples were identical. However, a big difference was evident when the samples were heated in boiling water for fifteen minutes, in a manner described in Section III. The cellulose sample was very superior. It had not darkened and was suitable for processing, while the sample dried with sodium sulphate was badly damaged. This difference was thought by the author to be due to adsorption of iron compounds by the cellulose. Sodium sulphate could not be considered as having any iron adsorption capacity.

X. An Acetylene Reaction Problem

It was thought that an insecticide intermediate could be made by
the reaction of acetylene and cyclopentadiene. This problem had
bothered the research people for some time, so it was decided that it
would be wise to try out the reaction on a small scale pilot plant.
In considering the reaction of these two materials, many interesting
possibilities occurred. First, both charges were capable of self-
decomposition and spontaneous explosion. Acetylene is a much more
dangerous material to handle than cyclopentadiene, but both materials
are energy rich. Also, if cyclopentadiene and acetylene will react,
it is extremely likely that hexachlorocyclopentadiene will react with
acetylene. These reactions describe the genesis of another patented
insecticide, aldrin. Most reactions resulting from either one of these
two charge materials, cyclopentadiene and acetylene, would be expected
to be highly exothermic. A reaction between these two should be tre-
mendously exothermic. The heat of reaction was beyond anything ever
observed by the author in his experience. The heat of reaction between
cyclopentadiene and acetylene was a considerable fraction, but still a
minor fraction, of some observed heats of combustion.

Again, the equipment cannot be described in detail. The type of
equipment to be used for such a reaction can be surmised from an article
discussing progress in acetylene chemistry in the last twenty years.[12]
In these discussions, it is suggested that acetylene spontaneous decom-
positions can be retarded or stopped by the filling of any reaction
space with standard one-fourth inch pipe lengths. The handling of this

(12) Hanford, W. F., and Fuller, D. L., Acetylene Chemistry, Industrial
     and Engineering Chemistry, pp. 1171-1177, July 1948.

apparatus required elaborate precautions including the placing of all pressure equipment, which contained acetylene, behind barriers of sand bags four feet wide and seven feet high. Several rupture disks and flame arrestors were used throughout the apparatus.

Before experimental work started, it was suggested by the author that atmospheric pressure reaction of these materials would be impractical, but that a pressure somewhere between 100 and 200 p.s.i.g. would give practical results. A proper temperature had to be found by experience, but the best temperatures for experimentation could be surmised from some of the work of Dr. J. W. Reppe, [13] among others, and by thermodynamical calculations. It is likely that this reaction may resemble ethynlation type reactions. According to Rossini, "Chemical Thermodynamics", [14] a reaction of this type could be diluted with a non-reactive gas such as nitrogen without any change in equilibrium constant except those changes in activity coefficients of the reactants, provided the partial pressure of the inert gas is not included in the total pressure used in equilibrium calculations. Also, according to Rossini, [14] an increase in pressure would definitely alter the equilibrium constant because two gaseous mols react to give one gaseous mol of product. For real gases, the effect of pressure on the concentrations of the reactants and products of a chemical reaction at equilibrium will also include the changes of the activity coefficients with pressure. This effect may be quite large. For example, in the equilibrium involving the synthesis of ammonia from hydrogen and nitrogen, activity coefficients have been known to change over

(13) Hanford, op. cit., pp. 1171-1177.
(14) Rossini, F. D., Chemical Thermodynamics, p. 354, 1950.

a wide range, with changes in pressure. Somewhat similar changes may be expected from the reaction of cyclopentadiene with acetylene.

When the pilot plant was put into operation, it was found that atmospheric reaction of acetylene and cyclopentadiene at any temperature tried was apparently impossible. Some reaction was possible at, say, fifty pounds pressure, but the reaction worked best in the range of pressure originally suggested and within the range of conditions tested.

Many problems were encountered in the experimental tests. Both acetylene and cyclopentadiene are capable of many side reactions, and formations of resins and carbon depositions were difficult to handle. It was found that expansion spots, between preheater and reaction zones, could not be allowed. These expansion spots, or enlargements, quickly filled with resinous materials and plugged off the charge lines completely. This plugging occurred because preheating was being performed in these lines leading to the main reaction zone. When the charge was adequately preheated and kept in the same sized lines leading to the reaction zone, many hours of reaction time could be logged before plugging occurred in the main reaction zone. However, the coil in this main reaction zone would always plug up with carbon or coke. If a run was made in a continuous fashion until the reaction coil plugged, best results were obtained. A very rapid and violent explosion of acetylene occurred, in only one instance. Its violence was quickly released by a rupture disc, and although much soot was scattered around the area, no fire resulted. The cause was not determined, and there was no recurrence.

Elaborate safety precautions were taken. As work proceeded,

equipment was greatly simplified. Much soot collected in the product condenser in the early stages. However, this tendency diminished as technique improved. One problem was the preheating of acetylene cylinders, as the main portion of the pilot plant work was done out of doors in very severe winter weather. Acetylene cylinder pressure was not adequate for operational purposes under these low temperature conditions. The acetylene cylinders used were the larger size of the welding supply type.

A probable heat of reaction was calculated by the author by the usual thermodynamical methods. When the work was completed, the data showed that the heat of reaction agreed remarkably well with that obtained in the reaction. The data obtained in the pilot plant work on this heat of reaction was not of the highest quality. Other quantities were more important in the particular investigation than the heat of reaction. Perhaps, actual agreement is not as close as that suggested by this data.

Much useful data for this investigation was obtained from an article discussing progress in acetylene chemistry. [15]

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(15) Hanford, op. cit., pp. 1171-1177.

XI. Summary

Solutions of many problems already outlined were achieved gradually by adequate thermodynamical calculations, followed by good design and good operational practice. A realization of the complex troubles, caused by metals contamination, came slowly. This point was quite forcefully brought home to the management in an accidental manner. From this time on, the development problems and their solutions fell into their proper places. Sometimes, it is difficult to grasp the importance of very small percentages of impurities.

Preparation of the purest possible charge materials was extremely necessary. This point was easier to grasp and was fairly quick in application.

Gradually, the idea of carrying on all reactions without a carrying solvent was applied. To sell this point was most difficult, but, when accepted, it was adopted with enthusiasm. After the adoption of this practice, much simplification was possible. About one-half of the equipment was discarded at this point.

Cleaning up steam and water problems was largely a matter of selling plant operations personnel on the value of better practices. Most of these ideas were well received, as their importance was easily appreciated by the practical men.

Solutions of problems in clean-up and drying of resin solutions and charges were rather simple, but sometimes, the ideas were a little difficult to sell. However, when an idea can be demonstrated by a simple and direct experiment, both practical and research men understand it readily.

Preparation of data required in the acetylene reaction problem was difficult. Much reading of pertinent literature was necessary. Many precautions were taken. This type of reaction must be treated with extreme respect. Actually, after the operation was set in order and much simplification of equipment done, these precautions might seem unnecessary. There are so many variables possible in this type of reaction that it is best to judge which variables are most important and act accordingly. Good intuitive thinking is quite useful at times for best solutions.

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VITA

Lawrence Ralph Hinken was born near Stover, Missouri, February 21, 1915, the son of William C. Hinken and Emma Evans. He graduated from high school at Holden, Missouri. In 1940, he was graduated from the School of Mines and Metallurgy of the University of Missouri with the degree of Bachelor of Science in Chemical Engineering.

He married Agnes Elizabeth Harlan of La Grange, Illinois, in 1943, and they have three children, Lawrence Ralph, John Albert, and Elizabeth Agnes.

His experience has been as follows:

Phillips Petroleum Co., Bartlesville, Okla., Chemist, 1940-1942.

Universal Oil Products Co., Des Plaines, Ill., Chemical Engineer, 1942-1946.

Velsicol Corporation, Marshall, Ill., Ass't. Development Chemist, Chief Plant Chemist, Ass't. Development Engineer, 1946-1951.

Bio-Process Co., Div. of Armour and Co., Industry Ave., Joliet, Ill., Chemical Engineer, 1951-.