

Expt. Chlorination

Still growing fast ...

Chlorinated Hydrocarbons

Allyl chloride, new high polymers, and vinyl chloride point to increasing demand for these versatile petrochemicals. New technology and production methods indicate most new plants will be based on petroleum derived methane, ethylene, and acetylene

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A BRIGHT FUTURE is predicted for the chlorinated hydrocarbon industry. Certainly some of the products will eventually fall by the wayside; others will have their production rates level off. Products which still have tremendous growth prospects are: (1) allyl chloride (expanding because of epoxy resin demand and the emphasis being placed on glycerine based polyurethane, and polyester resins; (2) the high polymers of fluorocarbons which are based on chlorinated hydrocarbons and (3) vinyl chloride which is just catching on in this country for structural and building materials.

A 1970 production of approximately 4.5 billion pounds per year of chlorinated hydrocarbons, or an increase of 1.3 billion pounds per year over the production in 1960, can be anticipated (Figure 1). At least 800 million pounds of this increased capacity will come from Gulf Coast installations.

PRODUCTION METHODS

When studying chlorinated hydrocarbon production methods and the

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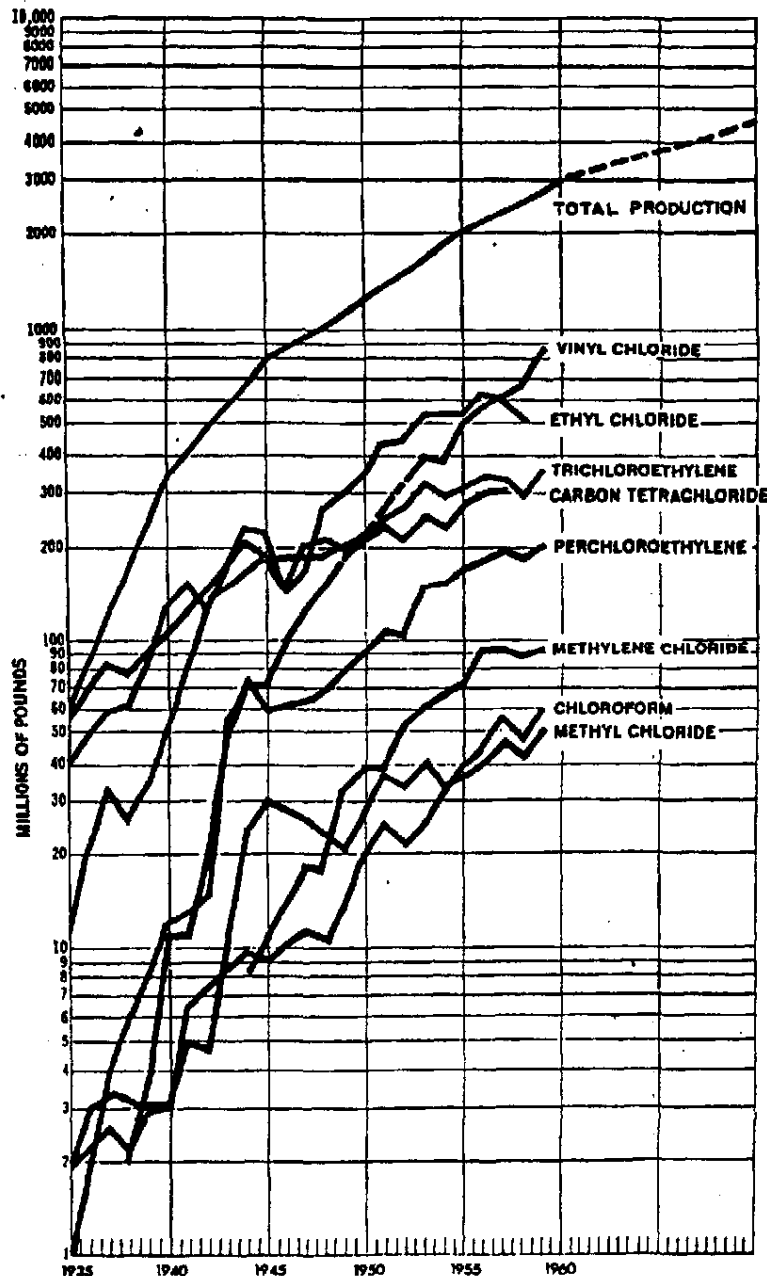


FIGURE 1—Here's how the various compounds fit into the overall picture. Notice that only ethyl chloride shows a definite down trend.

Chlorinated Hydrocarbons . . .

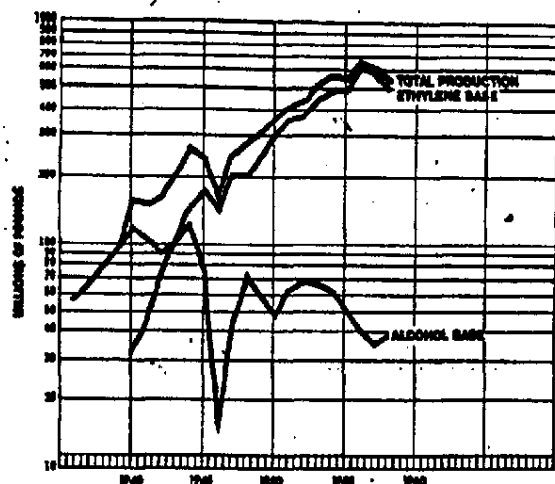


FIGURE 2—Shows United States ethyl chloride production. Notice that the original production was based on alcohol and in some areas alcohol raw material is still economically justified.

new and cheaper raw materials available, one point should be kept in mind: commercial ethylene from natural gas was not available in any quantity until the late 1930s and early 1940s and cheap acetylene from natural gas is still in the development stages. The data reported here include the various chlorinated hydrocarbons from coke, the sugar industry, calcium carbide, as well as the chlorinated hydrocarbons from the petrochemical sources.

The ethylene and propylene glycol families have not been considered here, though the chlorohydrin process is still a major source of glycol production.

Carbon tetrachloride, when introduced in the early 1900s, was made by reacting carbon bisulfide with chlorine. Today the majority of the United States' production is made by chlorination of methane, or as a co-product with perchloroethylene in a thermal chlorination process with hydrocarbon feed.

Chloroform, first produced by the reaction of bleaching powder and acetone or by the reduction of carbon tetrachloride with hydrogen and iron, is made today either by the chlorination of methane or the chlorination of methyl chloride, previously derived from methanol.

Methyl and methylene chloride are still produced today from methanol, but the major production is by methane chlorination.

MAJOR PRODUCTS

Ethyl Chloride. The original production (Figure 2) was based on ethyl alcohol. When ethylene from the

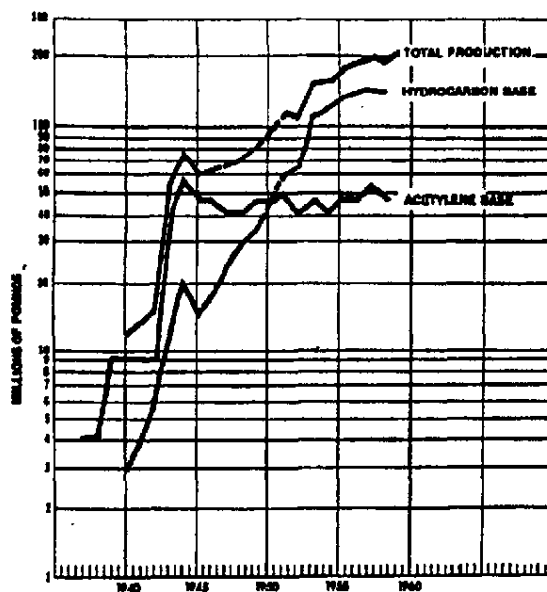


FIGURE 3—U.S. perchloroethylene looks like this with original production based on acetylene. However, thermal chlorination of hydrocarbon feeds such as methane, ethylene dichloride, propylene, etc. now accounts for the major production.

natural gas became available, new facilities were constructed to use this new raw material. Notice alcohol use continues today but only where justified by local conditions. Production data in this article is from U.S. Tariff Commission reports.

Perchloroethylene (Figure 3) originally was produced by the chlorination of acetylene-derived trichloroethane to penta chloroethane and subsequent dehydrochlorination with lime to perchloroethylene. Now it is produced primarily by the thermal chlorination of hydrocarbon feeds such as methane, ethylene dichloride, propylene, etc.

Vinyl Chloride, based on ethylene raw material was introduced in the late 1940s (Figure 4), but in contrast with the two previous products, the production from both raw materials is still growing.

Trichloroethylene, is the only commercial chlorinated hydrocarbon which remains tied to acetylene for the major part of its production. Acetylene is the same basic product and raw material from which it was produced originally. Figure 5 points out the impact of imports on this product, not a change in manufacturing techniques. Notice that during the last several years imports have had a drastic effect on the growth of production in the United States.

PLANT LOCATIONS

Production centers for these products have changed with the advances in process knowledge and new raw materials. Figure 6 shows what has happened since 1940.

Chlorinated Hydrocarbons . . .

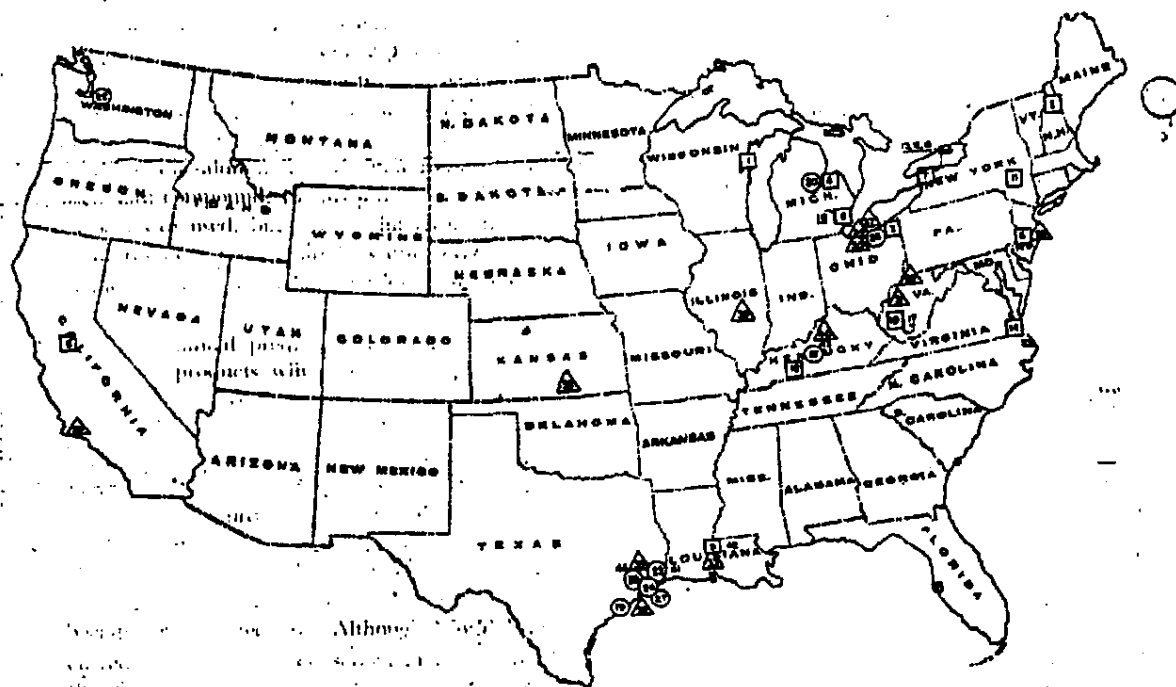


FIGURE 6—Here are the locations of chlorinated hydrocarbon plants in the United States.

In 1940, these plants were in operation: □

1. Anusol—Marinette, Wisc.
2. Brown—Berlin, N. H.
3. Diamond Alkali—Painesville, Ohio
4. Dow Chemical—Midland, Mich.
5. Dow Chemical—Pittsburg, Calif.
6. Du Pont—Deep Water, N. J.
7. Du Pont—Niagara Falls, N. Y.
8. Du Pont—Wyandotte, Mich.
9. Ethyl Corporation—Baton Rouge, La.
10. Food Machinery—South Charleston, W. Va.
11. General Electric—Watertown, N. Y.
12. Goodrich—Calvert City, Ky.
13. Goodrich—Niagara Falls, N. Y.
14. Hercules Powder—Hopewell, Va.
15. Hooker—Niagara Falls, N. Y.
16. Stauffer—Niagara Falls, N. Y.
17. Union Carbide—South Charleston, W. Va.
18. Wyandotte—Wyandotte, Mich.

In 1950 the following plants had come into operation: ○

19. Dow Chemical—Freeport, Texas
20. Dow Corning—Midland, Mich.
21. Goodrich—Louisville, Ky.
22. Hooker—Tacoma, Wash.
23. Jefferson Chemical—Port Neches, Texas

24. Monsanto—Texas City, Texas
25. Shell Chemical—Houston, Texas
26. U.S. Rubber—Painesville, Ohio
27. Union Carbide—Texas City, Texas

In 1960 these plants were added to the list: △

28. Allied Chemical—Moundsville, W. Va.
29. American Chemical—Watson, Calif.
30. Columbia Southern—Barberton, Ohio
31. Diamond Alkali—Bell, W. Va.
32. Diamond Alkali—Deer Park, Texas
33. Dow Chemical—Plaquemine, La.
34. Detrex—Astabula, Ohio
35. Ethyl Corporation—Houston, Texas
36. Frontier Chemical—Wichita, Kan.
37. General Tire and Rubber—Astabula, Ohio
38. Kolker Chemical—Newark, N. J.
39. National Petrochemical—Tuscola, Ill.
40. Stauffer—Louisville, Ky.

By 1961, these plants were planned or soon to become operational: ○

41. Columbia Southern—Lake Charles, La.
42. Monochem—Geismar, La.
43. Olin Mathieson—Doe Run, Ky.
44. Diamond Alkali—Houston, Texas

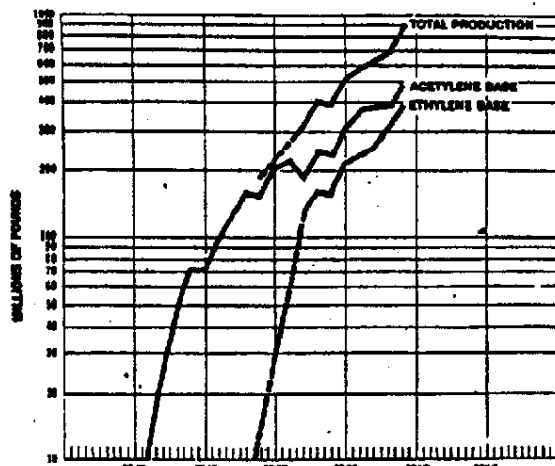


FIGURE 4—Notice the competition between acetylene and ethylene for vinyl chloride production with both growing rapidly.

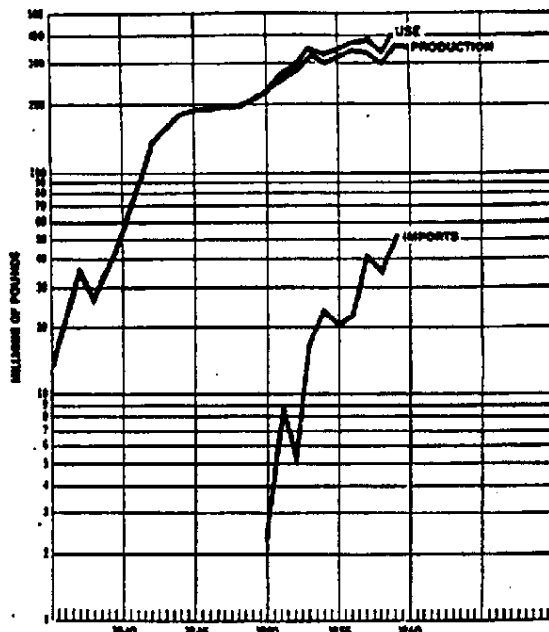


FIGURE 5—Trichloroethylene remains tied to acetylene for the major part of its production. However, notice the effect of imports on U.S. production.

By 1940 the total United States capacity for the production of chlorinated hydrocarbons was made up of 18 major plant sites in 13 cities. Of these only the Ethyl Corporation in Baton Rouge was located on the Gulf Coast.

One production location, Pittsburg, Calif., was the only plant then producing chlorinated hydrocarbons from natural gas based raw material. All other production was based on alcohols, calcium carbide based acetylene, carbon disulfide, and the like.

By 1950 the total number of plant sites increased to 27 in 19 cities, with the major growth on the Gulf Coast. Of the new plants, Dow at Freeport, Jefferson Chemical at Port Neches, Monsanto at Texas City, and Shell Chemical in Houston were using natural gas bases for these new products. Also Ethyl Corporation's Baton Rouge plant and Dow at Midland were switching part of their production to natural gas base. The Gulf Coast attracted these new plants because of abundant fuel, plentiful LPG feedstock, numerous salt domes, and the availability of water transportation.

By 1960 the number of plant sites increased to 40 in 29 cities. This growth resulted for three major reasons.

1. The use of methane as raw materials in the Ohio River area.

2. The expansion of vinyl chloride capacity in the Ohio River area by installing thermal cracking facilities to dehydrochlorinate ethylene dichloride to vinyl chloride and anhydrous hydrochloric acid. This will balance the hydrochloric acid needs on existing acetylene facilities for the production of vinyl chloride.

3. The installation of acetylene-HCl facilities for the production of vinyl chloride in localities where existing plants were modernizing their facilities for the production of trichloroethylene, making anhydrous hydrochloric acid a by-product rather than essentially throwing the hydrochloric acid away by cracking the tetrachloroethanes with lime.

Notable examples of this are General Tire and Rubber Company's Ashtabula, Ohio plant, which gets its anhydrous hydrochloric acid from Detrex's trichloroethylene facilities in Ashtabula, Ohio; and Goodrich's Louisville (Kentucky) plant, which installed thermal cracking facilities to balance the older acetylene-HCl facilities for the production of vinyl chloride.

Today there are some 44 major plant locations in the United States in 31 cities, producing chlorinated hydrocarbons. In 1960 these installations produced approximately 3,250,000,000 pounds of chlorinated hydrocarbons.

PRODUCTION CAPACITY

Figure 7 shows United States production capacity. The top line shows the summation of the published capacities for the production of chlorinated hydrocarbons and includes some plant capacity in stand-by condition only. It includes other plants that probably never will be run at design capacity again, because cheaper raw materials are available to produce the product more economically.

The second curve in Figure 7 shows actual production of chlorinated hydrocarbons over the same period as the top curve. The lower two curves show the pro-

"Chlorinated hydrocarbons should continue to grow despite annual predictions that production of individual products will drop off due to market saturation because new uses continue to appear which more than compensate for losses due to outdated uses"

duction capacity of the Gulf Coast vs. time and the production capacity of the United States less the Gulf Coast production vs. time.

The 1970 point of all these curves are dotted showing what could happen in the way of annual plant capacity in 1970 and showing what has already been announced in the way of increased capacities for 1970. The lower dotted lines include Columbia Southern's 100 million-pound-per-year ethylene dichloride plant in the Lake Charles, Louisiana area; it includes Monochem's, a company jointly owned by U.S. Rubber and Borden, announced plans for a 150 million-pound-per-year vinyl chloride installation to be located in the Gulf Coast area; it includes Olin Mathieson's new glycerine plant at Doe Run, Ky. Another expansion announced last summer is Diamond Alkali's multi-million-dollar expansion in Deer Park, Texas, to manufacture the acetylene requirements from natural gas and increase their vinyl chloride from 50 to 75 million pounds per year.

Figure 1 shows total chlorinated hydrocarbon production and individual compounds. The uses for these individual products have varied over the years by a very wide range. Some products, such as carbon tetrachloride and chloroform, whose major uses today are raw materials for the production of fluorinated compounds, were introduced originally as cleaning fluids, dry cleaners, pharmaceuticals, etc. Other products, such as ethyl chloride, have a questionable future, because of the advent of tetramethyllead as antiknock fluid in gasolines and because technology has introduced a new method using organic-aluminums as a new route to the much-used lead compound. In this process chlorinated hydrocarbons are used, but only as intermediates, and only small fractions are required as compared to the old method of using the ethyl chloride as the ethyl radical in tetraethyllead.

Despite annual predictions that production of these individual products will drop off, because of market saturation, and so forth, notice that ethyl chloride is the only one of these products through 1959 which shows a definite downtrend. It is very evident that the curve for the older products has a flatter slope than the curve of those products introduced in the 1930s and 1940s. To date, however, new uses for each of these chlorinated hydrocarbon products appear requiring a higher production rate than the loss in production rate because of outdated uses. Although World War II occurred during the period shown in Figure 1, and also the Korean conflict when special tax concessions were

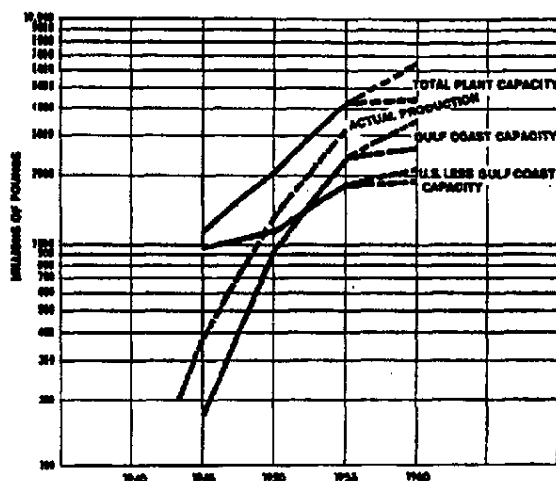


FIGURE 7—Shows a summation of production capacities for chlorinated hydrocarbons including some plants in standby condition and others not operating at design capacity. This is reflected by the actual production curve. Notice also the rapid growth of Gulf Coast production. Dotted lines show prediction of growth trends.

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issued for the manufacture of these products, neither of these events is obvious in the production patterns of chlorinated hydrocarbons.

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