

The Manufacture of Detergent Alkylate

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THE TERMS dodecylbenzene and detergent alkylate are used synonymously in the detergent industry.

Dodecylbenzene is the product prepared by alkylation of benzene with propylene tetramer. Most of the detergent alkylate suppliers are oil companies and, as such, are completely integrated from the production of crude oil to the manufacture of dodecylbenzene.



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Figure 1 shows the various steps in the production of detergent alkylate, which, as its name implies, is used almost exclusively for conversion to synthetic detergents.

The hydrocarbon raw materials for the production of dodecylbenzene are propylene tetramer or dodecene and benzene. Propylene has its origin in an oil refinery mainly as a by-product from catalytic cracking of heavy stock for the production of gasoline.

Benzene is also derived from a refinery operation designed for the preparation of high-octane gasoline. This operation is reforming. Benzene is also obtained from a much older source, the coking of coal.

Dodecene and benzene are combined to produce dodecylbenzene by catalytic alkylation, using a Friedel-Crafts catalyst. Fractionation of the crude alkylate into the desired boiling range is the final step in the production of the intermediate used to prepare approximately 500 million pounds of alkyl aryl sulfonates sold in finished detergents each year. The various steps and factors involved in the preparation of detergent alkylate will be considered in more detail in the following sections.

Propylene Tetramer Production

The fact that propylene tetramer is the main source of the alkyl groups in the alkylbenzene sulfonate type of detergents is probably more by accident than design. The advent of catalytic cracking shortly before and during World War II as a method of making high-octane gasoline introduced the problem of utilizing large amounts of low molecular weight olefins to the petroleum refiner. A very satisfactory method of upgrading gaseous propylene to gasoline was found to be catalytic polymerization. Since the products of

propylene polymerization are mono-olefins and since kerylbenzene sulfonates had opened the door to the synthetic detergent use of alkylbenzenes, it was logical that processes of making dodecylbenzene from benzene and propylene tetramer were developed. At least from a historical point of view it was a logical development.

Propylene containing about 50% propane and other saturated hydrocarbons is heated and injected into a catalyst chamber. The catalyst consists of pellets of kieselguhr impregnated with phosphoric acid or quartz chips coated with phosphoric acid. Polymerization conditions are approximately 1,000 p.s.i.g. and 200°C. The effluent from the polymerization unit is fractionated into three streams. Unreacted propane is the first, and this is used for fuel. Propylene trimer is the next fraction, and this is either recycled to the polymerization unit and converted to tetramer or used as motor gasoline, depending on the supply-demand situation. Some trimer is also used to prepare such chemical derivatives as nonylphenol and decyl alcohol. Propylene tetramer, the third fraction, is used almost exclusively for the production of detergent alkylate.

If the preparation of propylene tetramer were as simple and straightforward as just outlined, there would be few problems connected with the conversion to dodecylbenzene. Actually the chemistry of propylene polymerization is extremely complicated; in fact, polymerization is somewhat of a misnomer for the actual reactions which occur. Figure 2 shows some hypothetical reactions which might explain how some of the products are formed. Propylene is polymerized by a mechanism involving ionic intermediates. Addition of a proton from the catalyst to propylene

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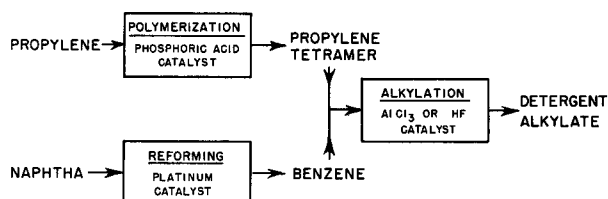


Fig. 1. Detergent alkylate production.

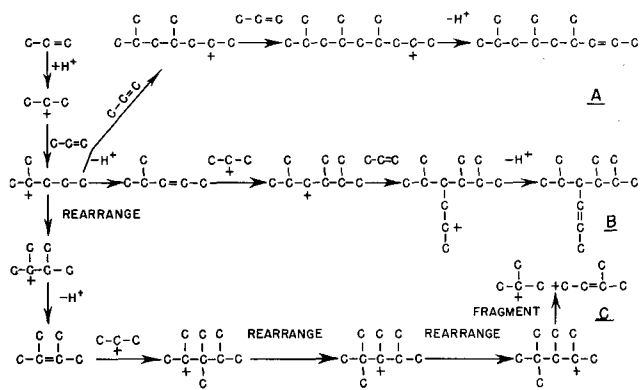


FIG. 2. Propylene polymerization reactions.

gives a carbonium ion which can be added to successive propylene molecules to give eventually the product shown as A in Figure 2. This molecule of dodecene might be called a true propylene tetramer. Probably very little of this isomer exists in the mixture known as propylene tetramer.

The route leading to product B involves a hexene isomer as an intermediate. To this is added the propyl carbonium ion, and the resulting ion then adds to propylene. Dodecene results from this route also, but it may be seen that dodecene B is structurally different from dodecene A.

To complicate matters further, the reactions leading to the intermediates labeled C also occur. Through rearrangement, elimination, and addition, fragmentation finally can occur to give a 4-carbon and a 5-carbon fragment. We thus have 3, 4, and 5 carbon number intermediates out of which olefins containing 7, 8, 9, 10, 11, 12, 13, 14, 15, etc., carbon atoms can be derived. Not only is it possible to have every homologue, but also it is likely that a large number of isomers are represented. Although propylene polymers are very complex structurally, they contain substantially 100% mono-olefins. Only traces of aromatics, saturates, and di-olefins are present.

The main specification for propylene tetramer is its boiling range. This has a large effect on the boiling range of the alkylate that can be economically derived by alkylation. Other specifications or properties of interest are bromine number, molecular weight, and contaminants.

Dodecene must be inhibited to prevent oxidation by air since this makes the product unsuitable for alkylation. The proof of a tetramer sample however is its behavior in the alkylation of benzene. Alkylation is used routinely to establish the quality of the tetramer. Table 1 lists some typical physical properties of propylene tetramer.

So much for the chemistry of propylene tetramer. Let us now consider the economic situation briefly.

Propylene tetramer has to compete for propylene with a number of other uses. Of the 1.7 billion pounds of propylene converted to chemicals each year, 500 million pounds are used to make tetramer. In spite of the greater upgrading in making chemicals rather than gasoline from propylene, there are still about 5.3 billion pounds per year used for fuel and gasoline. This indicates that there is an abundant supply of propylene for chemicals.

Benzene Production

The original large-scale industrial source of benzene, coke-oven operations, still accounts for a major amount of the benzene produced; but in the last decade petroleum benzene has become a large factor in the benzene market. As in the case of propylene polymerization, the need for higher octane gasoline was responsible for the production of benzene from petroleum. Benzene was known to have a very high octane number; but until the commercialization of reforming, benzene was not an economical fuel component in this country.

Reforming consists of dehydrogenating the naphthenes or cycloparaffins in virgin naphtha to aromatics. Probably the most popular process is platforming, which derives its name from the platinum catalyst which is used. Figure 3 illustrates the various

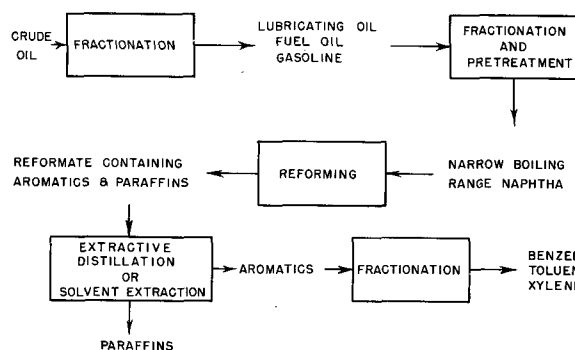


FIG. 3. Aromatics from petroleum.

steps involved in preparing and separating benzene. The naphtha is first treated to remove catalyst poisons and then is converted in the dehydrogenation unit. The platformate is used mainly as gasoline, but a good deal is processed for aromatics production. Aromatics are separated from paraffinic hydrocarbons by solvent extraction or extractive distillation. The aromatic concentrate is then fractionated into benzene, toluene, and xylene.

The supply of petroleum benzene is nearly unlimited, but the ratio of chemical benzene to fuel benzene is determined by many factors. Among these factors are the production of benzene as a by-product of coke manufacture, the increasing octane number requirement of gasoline, price, and purity. Purity is becoming less of a factor as coke oven operators are installing purification facilities similar to those employed by petroleum refiners.

Detergent Alkylate Preparation

Although most of this section will deal with the present-day production of dodecylbenzene, a little history may put dodecylbenzene into the proper perspective. The reactions by which alkylbenzenes are produced today are by no means new. Pioneering work by Friedel and Crafts established that benzene could be alkylated many years ago. Alkyl halides, alcohols, and olefins were found to be suitable alkylating agents, but until recently these materials were economically unavailable.

The first major detergent alkylate was keryl benzene. Keryl benzene was and still is produced by

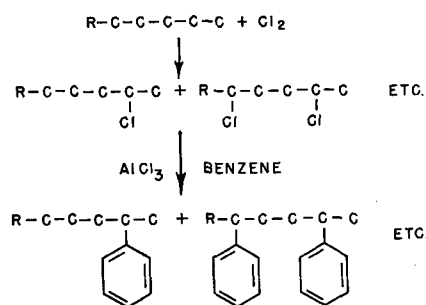


FIG. 4. Kerylbenzene reactions.

chlorination of a kerosene fraction, followed by alkylation of benzene with the alkylchloride. Aluminum chloride is used as the alkylation catalyst. Figure 4 outlines the reactions that take place. Chlorination of a paraffin mixture, such as kerosene, is non-selective in that it is as easy to di- or trichlorinate as it is to monochlorinate; therefore low chlorination conversions are necessary to prevent dichlorination and the subsequent alkylation of two benzene molecules. Side reactions are also prevalent, and relatively poor yields result. Keryl benzene established the value of alkylbenzenes as detergent intermediates, and the need for an easily purified, cheap alkylbenzene was evident. Dodecylbenzene seems to have filled this need.

Production of high-octane gasoline components gave petroleum companies all the hydrocarbon raw materials and skills necessary to make dodecylbenzene-benzene from reforming operations, propylene tetramer from catalytic polymerization, and alkylation know-how from the manufacture of aviation alkylate. In retrospect, the process for making detergent alkylate was a very logical development. I am sure that there were some grave misgivings and unknown factors while the process was being developed.

Figure 5 shows the chemistry of dodecylbenzene synthesis, which is quite simple on paper. In actuality, the reactions that take place are complicated and numerous. The reaction of interest consists of the addition of benzene across the double bond of the olefin to produce the desired alkylbenzene. Means of minimizing the amount of by-products formed introduces the complicating factors.

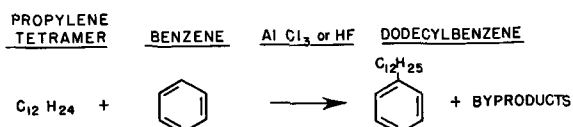


FIG. 5. Dodecylbenzene reactions.

Figure 6 is a flow diagram for a detergent alkylate plant. This, of course, is a great over-simplification. Figure 7 shows a photograph of Continental Oil Company's detergent alkylate plant at Baltimore, Md. It is obvious that the plumbing is quite complicated.

The heart of the dodecylbenzene process is quite naturally the alkylation step. In this step the catalyst, the mole ratio of benzene and tetramer, and conditions of temperature, time, and pressure are the factors that must be controlled to produce good results.

Catalysts used today for the alkylation step are hydrogen fluoride and aluminum chloride. Only one of the major alkylate producers uses hydrogen fluor-

ide. The others use AlCl₃. Conditions for the two catalysts are not greatly different except that hydrogen fluoride is used in much greater than catalytic amounts and is recovered and recycled. Aluminum chloride is used in catalytic amounts, requires a promoter such as water or hydrogen chloride, and is not recovered for recycle since it becomes deactivated. It is necessary to use a large excess of benzene of the order of 5 to 10 moles per mole of tetramer to minimize side reactions. These will be discussed later. Temperatures used for the alkylation reaction range from room temperature to about 50°C. Residence times vary from minutes to about one hour, depending on whether the reaction is run continuously or batchwise. With HF as the catalyst it is necessary to operate at a moderate pressure to keep the catalyst in the liquid phase.

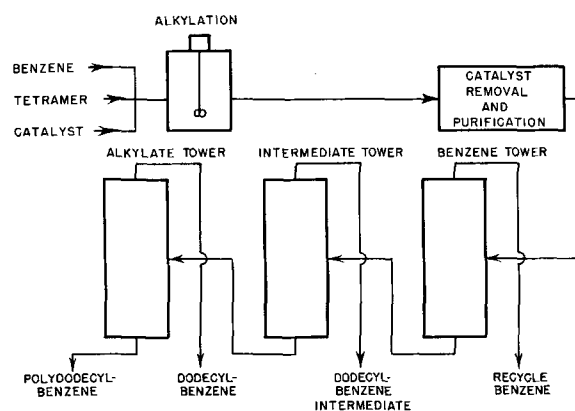


FIG. 6. Detergent alkylate plant.

Following the alkylation reactor, the crude product is purified. With HF catalysis the catalyst is separated for reuse. With AlCl₃ catalysis the catalyst complex is removed. The hydrocarbon mixture is treated to remove acidic impurities and is then separated into four components by fractional distillation. Excess benzene is the first component removed, and this is recycled to the alkylation. The benzene-free alkylate contains low molecular weight alkylbenzenes formed as by-products. These compounds are called

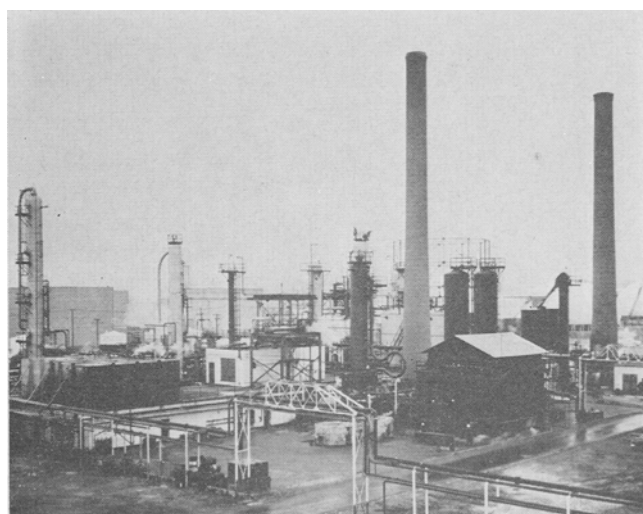


FIG. 7.

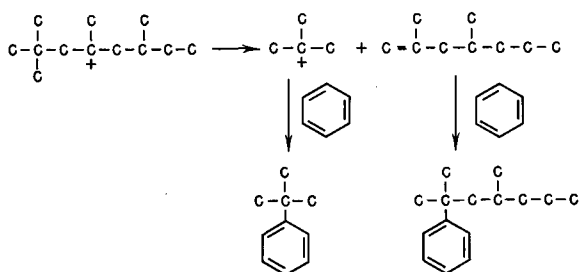


FIG. 8. Fragmentation reaction.

dodecylbenzene intermediate and are removed as the next fraction. Dodecylbenzene is the next fraction taken overhead and represents the primary product of the process. Polydodecylbenzene, another by-product, is recovered from the process as a bottoms fraction.

As was mentioned above, the chemistry of the reaction to produce dodecylbenzene from tetramer and benzene is fairly simple, but the side reactions introduce complications. The problem is to maximize the main reaction and to minimize side reactions. Catalysts such as HF or AlCl₃ will not only catalyze alkylation but also will catalyze polymerization, isomerization, fragmentation or depolymerization, and disproportionation of the propylene tetramer. In these side reactions, HF and AlCl₃ are similar to the acidic catalyst used originally to polymerize propylene.

Since almost all of the side reactions involve reactions of the propylene tetramer, a large excess of benzene (5 to 10 moles per mole of tetramer) is used. The high concentration of benzene tends to favor the desired alkylation reaction and to lessen the chance that side reactions will take place. Another side reaction not mentioned is dilakylation of benzene. This is one reaction by which polydodecylbenzene is formed. The excess of benzene shifts the equilibrium in favor of monododecylbenzene, the desired product.

Polymerization of propylene tetramer by the alkylation catalyst results in olefins containing about 24 carbon atoms. Upon alkylation with this high molecular weight olefin, a high molecular weight alkylbenzene results. Although high molecular weight alkylbenzenes were originally undesirable by-products, oil-soluble sulfonates prepared from these compounds and used as lubricating oil detergents have made polydodecylbenzene a valuable coproduct.

Isomerization of tetramer by the catalyst undoubtedly occurs, but this is believed to be relatively unimportant. Since the olefin has been so highly isomerized

by the polymerization catalyst, isomerization during the alkylation reaction cannot worsen the situation very much.

Fragmentation is a serious side reaction in that it degrades benzene and propylene tetramer to products of low value. A fragmentation reaction was described in the section on tetramer production. Another example is shown in Figure 8; thus, from the fragments, alkylbenzenes below those useful in detergent alkylate are produced. A loss of yield of between 10 and 15% is sustained in the production of dodecylbenzene intermediate; however not all of this by-product is formed by fragmentation reactions.

The other reaction that produces dodecylbenzene intermediate is disproportionation (Figure 9). The result of this disproportionation is the production of undesirable saturates and polyolefins which are both undesirable. The saturate produced by disproportionation and the low molecular weight aromatics formed by fragmentation are found in about equal amounts in dodecylbenzene intermediate.

Dodecylbenzene, as marketed, is a mixture of many alkylbenzenes, but components other than alkylbenzenes are present in low amounts. The main impurity is a component that makes up a major part, but not all, of the free oil found after sulfonation and neutralization. This component consists of saturated aliphatic hydrocarbons. It is similar to the saturates found in dodecylbenzene intermediate except that the saturates in dodecylbenzene fraction have a higher molecular weight. These saturates are formed by consecutive reactions of polymerization and disproportionation.

Other impurities, such as olefins, are present in only trace amounts. In the decade that detergent alkylate has been marketed, there has been a steady increase in product purity. This has resulted in lower free oils, lighter color, and less odor in the finished sulfonate. Not only has a reduction in impurities been accomplished, but also the boiling range of the alkylate has been narrowed.

Since detergent alkylate is such a mixture of isomers and homologues, it is impossible to define very narrow specifications for the product. For instance, a boiling range is specified instead of a boiling point. Quite naturally over the years the boiling range of detergent alkylate has been narrowed to improve the properties and purity of the finished sulfonate. It was desirable to have the initial boiling point as high as possible since the free oil components seem to concentrate in the front end. The final boiling point was lowered to eliminate impurities that cause color and odor in the finished sulfonate. Table I also shows some typical physical properties of detergent alkylate.

Although the narrower boiling range of the alkylate meant higher purity to the detergent manufacturer, it

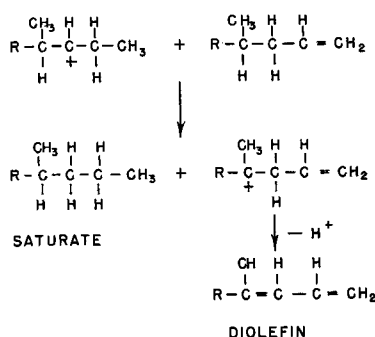


FIG. 9. Formation of saturates and olefins.

TABLE I
Physical Properties

A.S.T.M. Distillations (°F)	Tetramer D-86°F.	Alkylate D-158-41°F
I.B.P.	349	535
5%	357	545
10%	359	550
50%	374	560
90%	412	580
95%	433	592
E. P.	457	603
Bromine Number	110	0.1
Molecular Weight	163	237
Saybolt Color		29 +

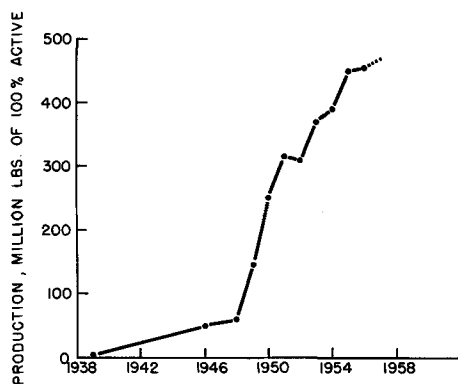


FIG. 10. Production of alkylarylsulfonates.

meant lower yields and consequently higher costs to the alkylate producer. Since quality and profits were opposing factors, the narrowing of the boiling range has been a gradual change. Another reason for the gradual change is the relation between the boiling range of the propylene tetramer and the detergent alkylate. From a quality standpoint, the boiling range of the alkylate and the boiling range of the olefin need to be matched. This matching can be done only by trial and error, and a great many factors enter into the situation. For instance, use tests such as detergency, foaming characteristics, etc., had to be evaluated before a major change was made.

So much for the technical side; let us now consider the economic situation briefly. Figure 10 shows that the growth of alkylbenzene sulfonates has increased tremendously in the last 10 years. Figure 11 shows that there has also been a considerable decrease in price over the last 10 years. There is a marked correlation between the price and growth curves.

It appears that both price and production are levelling out. Since the initial gains in detergent alkylate business resulted from displacement of soap and since this displacement has proceeded nearly to a stable balance, it is likely that alkylbenzene sulfonates will grow as new uses are developed and as the population increases. Another market for detergent alkylate, the export market, is stabilizing. The reason is that detergent alkylate plants are coming on stream abroad and will supply the additional demand in the areas in which they are located. The price of detergent alkylate was initially quite high but has decreased to the present price of 11.7¢ per pound. At the present price level, raw material costs make up approximately two-thirds of the selling price of dodecyl benzene. This means that detergent alkylate suppliers are operating plants, amortizing equipment, and obtaining profits from the remaining third. The decrease in price from 20¢ a pound in 1948 to 11.7¢ a pound in 1958 indicates, for one thing, that alkylate

manufacturers have learned a great deal in the last 10 years.

Just because price and production are levelling off does not mean that alkylate production is becoming static. One field of detergent use that has not been appreciably affected by synthetic detergents is toilet bars. Recently toilet bars containing synthetic detergents have shown marketing promise. An alkylbenzene sulfonate suitable for use in toilet soaps will probably come into commercial existence in the near future. The use properties of dodecylbenzene sulfonates, although satisfactory as judged by the volume used, are not ideal for every use. It is likely

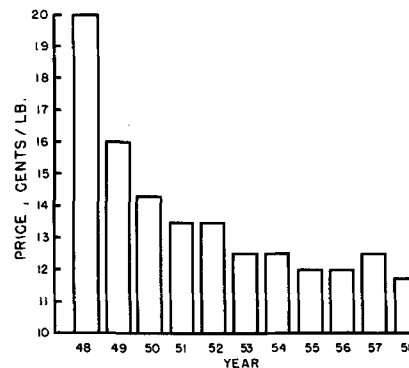


FIG. 11. Price of dodecylbenzene.

that the future will see a variety of alkylbenzene sulfonate products designed for more specific uses. To accomplish this, the properties required for the use must be known, methods of testing or screening new products must be developed, new compounds must be made and tested, and new theories must be formulated and tested. All of this is a continuing process that leads to progress.

A problem that will have to be faced in this country sooner or later is the trouble caused in sewage disposal by alkylbenzene sulfonates. This problem is already serious in Europe where water reuse is more extensive than it is in the United States.

Research will not only solve the problems that exist in the manufacture and use of detergent alkylates but also will provide products of greater usefulness. Our free enterprise system makes it a necessity that a business improve its products and services. Doubtless every detergent alkylate producer realizes that 10 years from now much better products will be on the market and that, unless he has a hand in bringing about these improvements, he is going to lose his share of the business. The next decade in the history of detergent alkylate will undoubtedly be as interesting and challenging as the previous one has been.