

Detergents Continuously

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ON THE AVERAGE, each American will use some 20 pounds of synthetic detergents this year. Most will be solid types and, chances are, per capita consumption will likely reach some 23 pounds annually by 1960. In marked contrast, syndets were a scant part of household and personal cleansing materials 12 years ago.

That was when syndets began their meteoric rise. World War II was over and chemical process facilities freed again for civilian use. Incentives were strong to develop and market synthetic detergents. Vast potentials existed in virtually every area where soap or soap products were used—shampoos, laundry products, dishwashing materials. Only bar soap seemed immune to a detergent envelopment, but now time has caught up here and syndets have a foothold in this area as well (5).

This year, the soap and detergent industry will sell roughly 3 billion pounds of detergents—almost a 700% increase in a decade. More than half of the total tonnage of detergents made annually in the United States are alkylaryl sulfonates (9).

Sales of syndets, both solid and liquid types, now represent nearly 72% of the total market for soaps and detergents in the U. S. (2). Ranking among the outstanding triumphs for syndets is the consumer acceptance of household packaged laundry and dishwashing products. Almost nothing in 1946, synthetic detergents now take in 90% of this market.

But the syndet market is no longer in a rapid growth stage. Maturity has set in and the market is perking along at about a 4% annual growth rate. Syndet

infiltration into bar soaps, however, may accelerate this pace in the short-term future.

And, liquid detergents are gaining too. They now take in about 10% of the total detergent business and the future outlook is very bright.

P & G Played Major Role

Throughout the syndet growth period, Procter & Gamble played a major role in developing, producing, and then promoting detergents. P & G scored a major technological gain when it again upset the soap industry's traditional "batch process" concepts by making detergents through continuous processes (4, 8). Sulfonates, sulfates, and variations poured from P & G's manufacturing facilities and when mixed with appropriate builders, dyes, and the like were enroute to market as Tide, Cheer, Dreet, and other washing products.

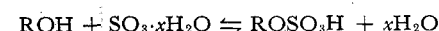
To make a continuous process work commercially, P & G's scientists had to

work carefully with the laws which govern chemical equilibrium. Sulfation, in particular, is a ticklish problem. Conditions must be controlled carefully to maximize yield and minimize side reactions.

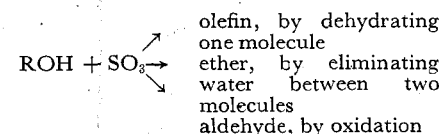
P & G makes alkyl sulfates from tallow fatty alcohols (C_{16} and C_{18}). Conversion to the corresponding sodium alkyl sulfate involves a two-step process: sulfation, then neutralization, both by conventional chemical reactions (10). The company could use many sulfating agents, such as sulfuric acid, stabilized sulfur trioxide, chlorosulfonic acid, and oleum. P & G uses oleum because it is economical and it was readily available when P & G started to make detergents continuously, some 22 years ago. To this day, oleum has proved its worth in plant practice and P & G expects to continue using oleum for some time to come.

Also, oleum is more effective than sulfuric acid and avoids the HCl disposal problems of chlorosulfonic acid and the handling problems inherent in sulfur trioxide.

In sulfation, the desired reaction is to form the monoalkyl sulfuric acid ester:



The reaction is rapid and must end quickly. Oversulfation can occur via a number of side reactions:



Further oxidation of the aldehyde will make an acid which would be esterified by the fatty alcohol (11). Still other side reactions are also possible, such as isomerization, carbonization, and chain cleavage.

Excess reaction times—or temperatures—will promote the olefin, ether, and aldehyde side reactions. Pilot plant tests by P & G prove this point. There is an optimum set of conditions for sulfation. Beyond this point, yield and product deteriorate rapidly (Figure 1).

Conversely, at less than the maximum conditions, sulfation will fail to reach equilibrium. The equilibrium point is determined by the free-water concentration in the reaction mix. Because water is released as SO_3 is consumed, excess acid is required to keep the water concentration low. Oleum helps to cope with this problem. It has a lower initial water content than sulfuric acid; hence, P & G can use considerably less oleum than sulfuric acid, and still get the same degree of sulfation.

Sulfonation Easier

Whereas sulfation is a tricky process, sulfonation is rather straightforward and

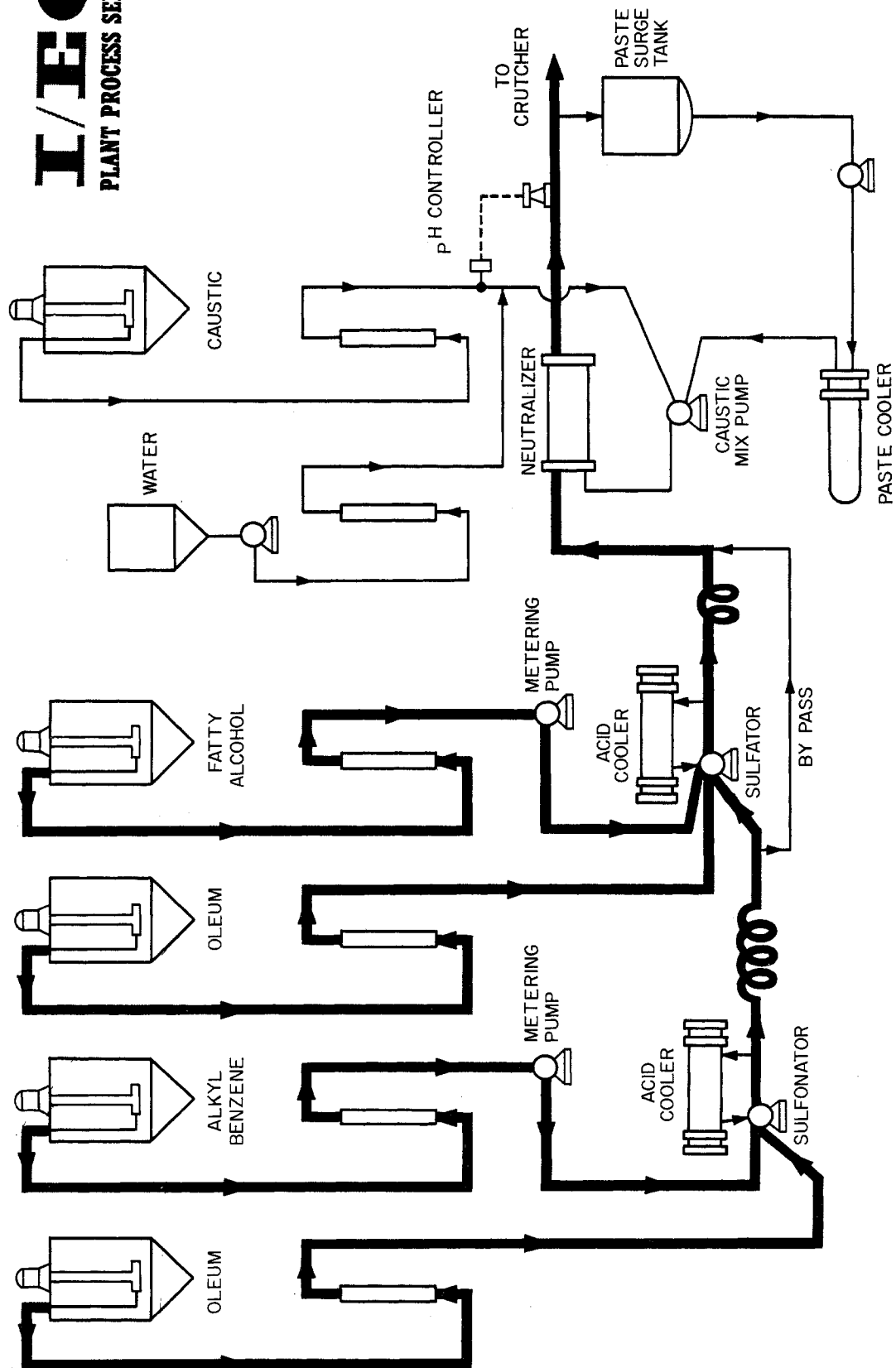
Detergents Keep Growing

Year	Thousands of Pounds (1)		
	Liquids	Solids	Total
1948	709	401,154	401,863
1949	10,320	702,136	712,456
1950	22,560	1,070,628	1,093,188
1951	38,224	1,217,022	1,255,246
1952	49,600	1,480,519	1,530,119
1953	94,696	1,772,187	1,866,883
1954	118,792	1,944,484	2,063,276
1955	153,008	2,164,470	2,317,478
1956	259,656	2,430,671	2,690,327
1957	363,480	2,552,286	2,915,766
1958 ^a	404,000	2,496,000	2,900,000

^a Estimated.

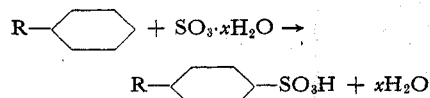
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PLANT PROCESS SERIES



Flowsheet of process to make sulfate and sulfonate detergents continuously, Procter & Gamble Co.

causes few problems. Oleum reacts with alkylbenzene to form an alkylbenzene-sulfonic acid.

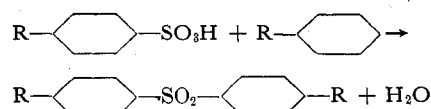


The reaction is not reversible and follows a smooth time-temperature curve. Once the reaction peak is reached, neither higher temperatures nor longer contact times will materially alter the degree of sulfonation (Figure 2).

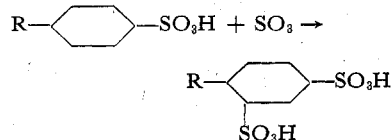
Water will not create a problem. But a certain excess of acid is needed to keep the residual acid strength above 95% because little or no reaction takes place with weaker acid. Caution is needed to keep a proper balance of excess acid, for side reactions can cause color bodies that darken the product.

Also of some concern are secondary reactions which can take place:

Sulfones



Disulfonates



By reacting oleum and alkylbenzene under proper conditions, however, these secondary effects are limited to less than 0.1% of the final product.

Following sulfonation and/or sulfation, the acid mixes are neutralized with caustic soda to form the corresponding sodium salts:

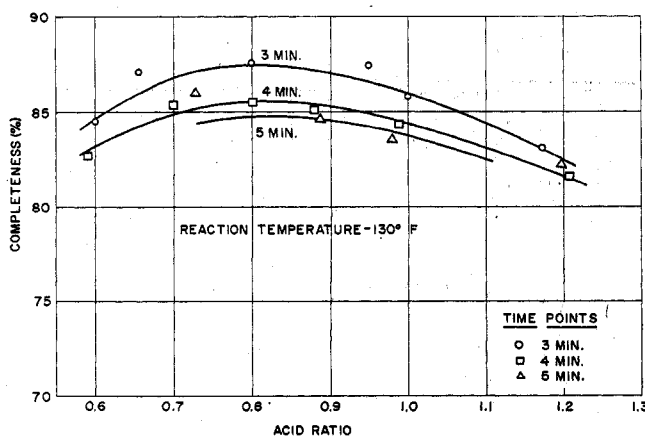
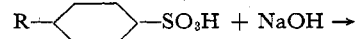
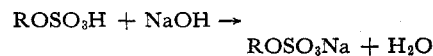


Figure 1. Sulfation

Brief Look at Detergent History and P & G's Role

Synthetic detergents are an outgrowth of a long standing textile industry problem—need for a surface active agent which would work in hard and acidic waters. Until 1920, sulfated turkey red oil was the best available, but then, German researchers developed an alkyl naphthalene sulfonate. This product was a good wetting agent but it had little detergent value (7).

A decade later, H. T. Böhme, A. G., had a new concept: a fatty alcohol sulfate, trade-named Gardinol. It was made by sulfating fatty alcohols from high pressure hydrogenation of fatty acids. About the same time, I. G. Farbenindustrie started to market fatty acid esters of hydroxyethanosulfonic acid. But these German efforts were aimed at industrial, not consumer markets.

Soon after Böhme started to sell Gardinol, the German firm signed a marketing agreement with National Aniline, which offered the product to American firms. By 1932 Du Pont and Procter & Gamble also made arrangements with Böhme and started to make fatty alcohol sulfates through the jointly owned Gardinol Corp. Du Pont's interest was mainly industrial whereas P & G's was in the consumer field.

The first product offered the consumer was P & G's Dreft, introduced 25 years ago. It was a sodium alkyl sulfate made from chlorosulfonic acid and a fatty alcohol via a batch process. By 1937, P & G converted the process to a continuous method using sulfuric acid and a coconut fatty alcohol (C₁₂ to C₁₈ range). The process and product remained until World War II when the Government took over fatty alcohol production to make dodecylmercaptan for the war effort.

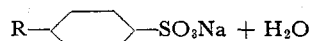
During the war, P & G managed some research on continuous detergent processes but for the most part, commercial practices remained unchanged. But during the war years, two developments occurred which were to change the future of detergents (3).

• Alkylbenzene came along. This gave soap makers a raw material which would make the manufacture and sale of detergents competitive with soap products.

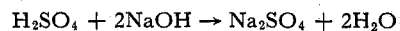
• Tripolyphosphates were shown to be useful builders in detergent compositions, particularly for heavy duty detergents.

Products such as Dreft were light duty and not suited for the family wash. Heavy duty detergents were needed and tripolyphosphate in combination with the various surface active agents was the answer.

In 1946, P & G turned to oleum sulfonation and sulfation via a continuous method which opened a new concept in volume production of detergents.



Excess sulfuric acid is converted to sodium sulfate:



The sodium sulfate formed is an inert

material and is left in the final detergent product. There are cases, however, where it is desirable to include less sodium sulfate than that normally made through neutralization of the sulfonate acid mix. This then involves use of a layering step where water is added to the

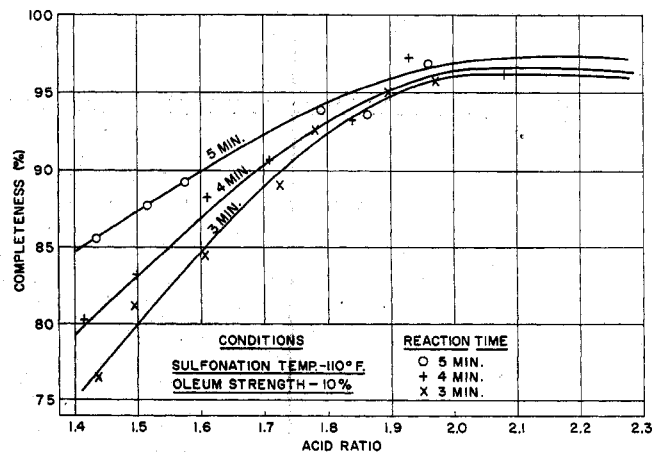
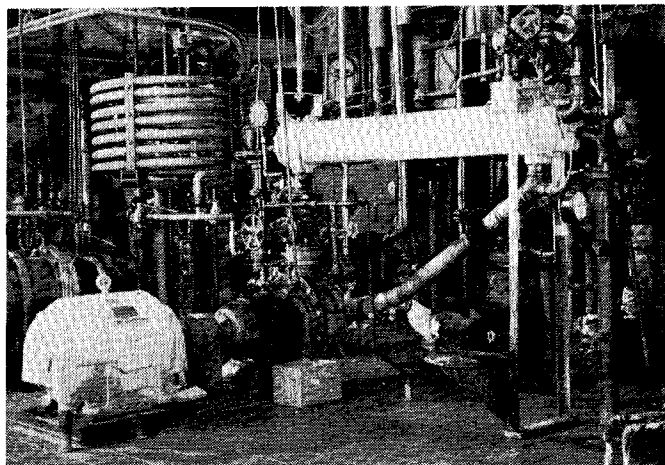
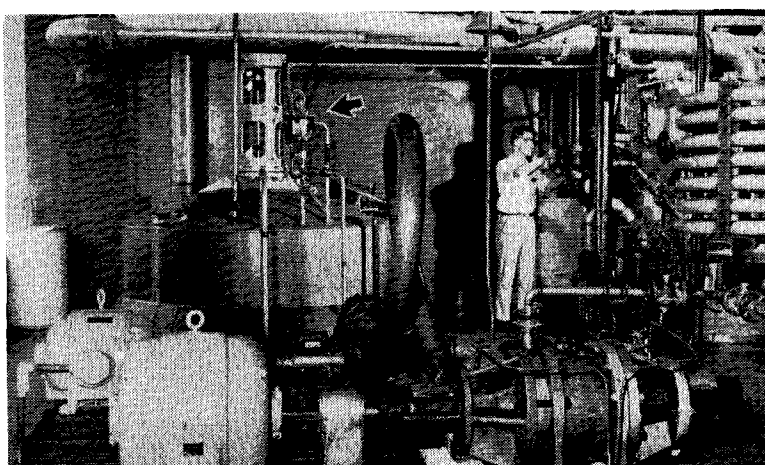


Figure 2. Sulfonation



Slurry from reactions is passed to neutralizer system—also a dominant bath. Caustic soda is used to neutralize acid mix—amount added controlled by a pH controller (arrow)

Key to P & G's continuous processes is dominant bath, such as this one for alcohol sulfation. The bath consists of a mixing pump and small heat exchangers

The switch to a continuous detergent process gave P & G many advantages over the traditional batch process methods

- Shorter reaction times and better color of product
- Higher throughput rates with less equipment
- Better control of the operation and less variation in the final product
- No HCl disposal problems—common to the chlorosulfonic acid batch process
- Reduced manpower needs

acid mix before neutralization. After settling, the top organic layer is neutralized to form the desired product. Layering increases sulfonate to sodium sulfate ratio in the neutralized material from 1 to 1 to about 8 to 1.

Made in Many Plants

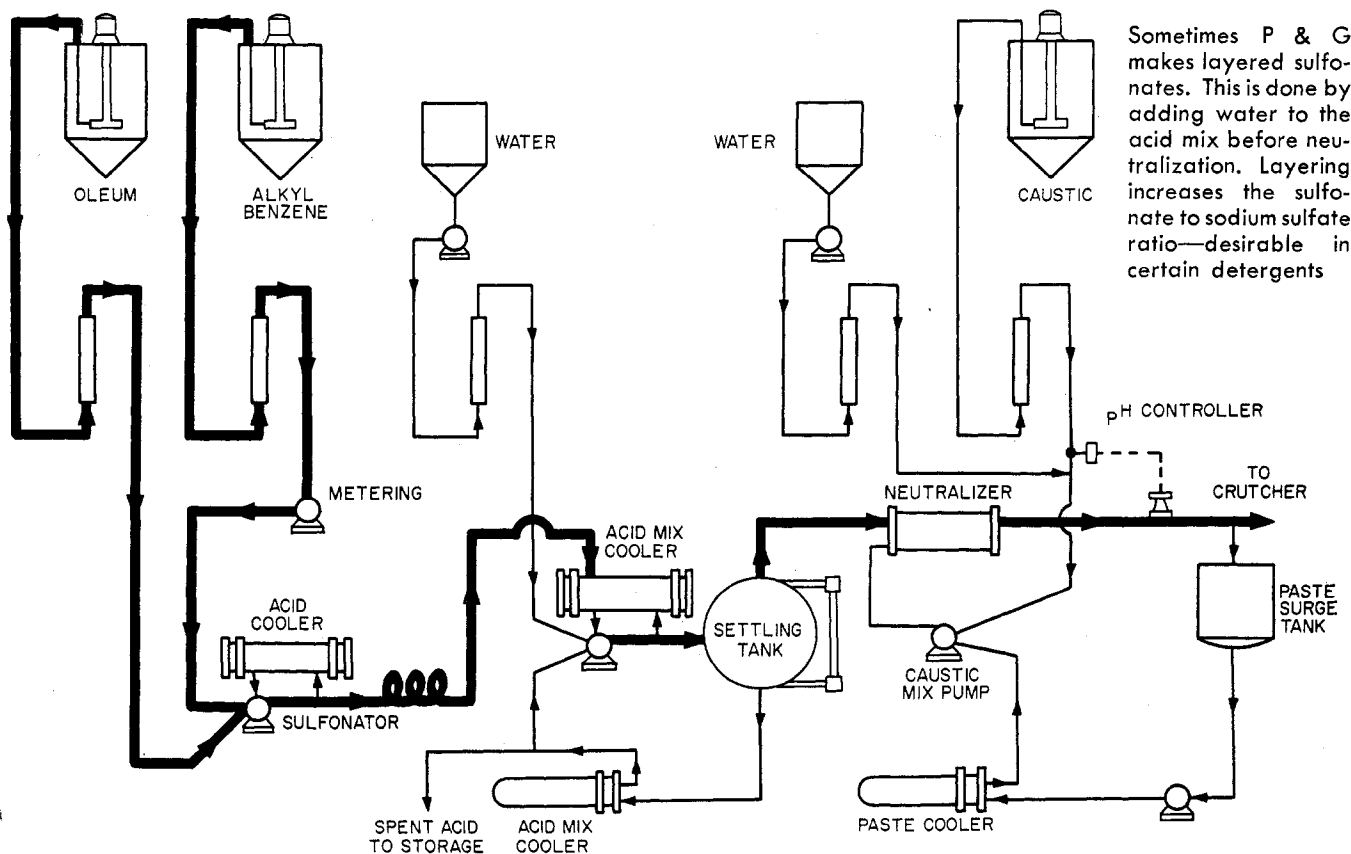
Procter & Gamble makes sulfates and sulfonates (and variations) at its Port Ivory (Staten Island), N. Y., plant, subject of this article. In addition, the detergents are made at Quincy, Mass.; Baltimore, Md.; Chicago, Ill.; Cincinnati, Ohio; Kansas City, Kans.; St. Louis, Mo.; Dallas, Tex.; and Long Beach and Sacramento, Calif., plus overseas locations. All plants use essentially the same process equipment.

Features of this equipment are simplicity

and the flexibility it gives P & G. These units are divided into two major loops or "dominant baths." All parts are stainless steel. The reaction bath consists of a mixing pump and heat exchanger (only 8 inches in diameter and 5 feet long). Into this bath are pumped oleum and feed stock—alkylbenzene for sulfonates, fatty alcohol for sulfates. The neutralization bath is a mixing pump, a heat exchanger (2 units, each about 2.5 feet outside diameter and 20 feet long), a neutralizer, and surge tank.

These units allow P & G to make four different types of detergents at its plants:

- Alkyl sulfates.
- Alkylarylsulfonates.
- Mixed alkyl sulfates and alkylaryl-sulfonates.
- Layered alkylarylsulfonates.



The key raw materials needed—oleum, fatty alcohol, alkylbenzene, and caustic soda—are either purchased locally by P & G or made by the company.

The liquids are stored on a tank farm adjacent to the processing building. These tanks have sump pumps which provide the pressure for the process piping system. Pumps are controlled from the process panel board in the immediate processing area.

Sulfonate Processing

When making alkylarylsulfonates, alkylbenzene and oleum (10 to 25% depending upon final product) are pumped from storage at a rate of roughly 100 to 125 pounds of oleum to each 100 pounds of alkylbenzene. The liquids are metered to a centrifugal pump which provides the first mixing step. The pump shoots the acid mix around the "dominant bath"—the loop formed by the pump and heat exchanger.

But the mix circulates through the shell rather than the tubes of the exchanger.

The heat transfer coefficient is excellent, hence a small exchanger can be used. This cuts down the volume of material which circulates at any given moment.

Water circulates through the exchanger tubes to cool the highly exothermic reaction. Temperatures of the reaction are controlled to 120° to 130° F. The oleum and feed stock are fed to the loop at rates to meet production demands.

The intermediate formed—alkylbenzene sulfonic acid—is removed from the dominant bath in a ratio of one part taken off to 20 parts circulating. It is then passed through a coiled pipe or "delay step" to ensure complete conversion to the intermediate.

Process Control and Analyses

P & G sets rigid specifications for all raw materials received and final products made. Incoming materials are analyzed for proper specifications—for example, with oleum, a check for total H_2SO_4 content.

Specific gravity of the reaction mix equivalent is used to control the proper ratio of acid to alkyl benzene (or fatty alcohol). If the value is outside limits, a correction is made in the ratio of raw materials.

Finished detergent slurry is analyzed during each shift for moisture and active detergent content. Also, materials are checked for sulfation or sulfonation completeness.

P & G Makes Its Own Fatty Alcohols

Fatty alcohols in the C_8 to C_{18} range are made by P & G at Sacramento, Calif., and Kansas City, Kans. However, only those in the C_{12} to C_{18} range are used to make alkyl sulfates. Until 4 years ago, the sodium reduction route was the main path to P & G's fatty alcohols, but now this method has been replaced with the newer catalytic hydrogenation process (6).

In this process, a fat—coconut oil or tallow—is converted to the respective methyl esters, with glycerol as a by-product. The latter is removed for sale while the esters go on to the reduction step.

This takes place in laminated prestressed reactors. Hydrogen pressures vary from 3000 to 4000 p.s.i., depending upon purity of the feed. A copper-chromium catalyst (Adkins type) is used. Hydrogen comes from a packaged hydrogen plant.

During reduction, methanol splits off and fatty alcohols are formed. Unsaturates are hydrogenated, because for detergent manufacture the alcohols must be saturated.

Process reactants are re-used in the process while the fatty alcohols are fractionated. Alcohols in the C_8 to C_{10} fraction are sold to plasticizer makers.

Alkylbenzene Manufacture

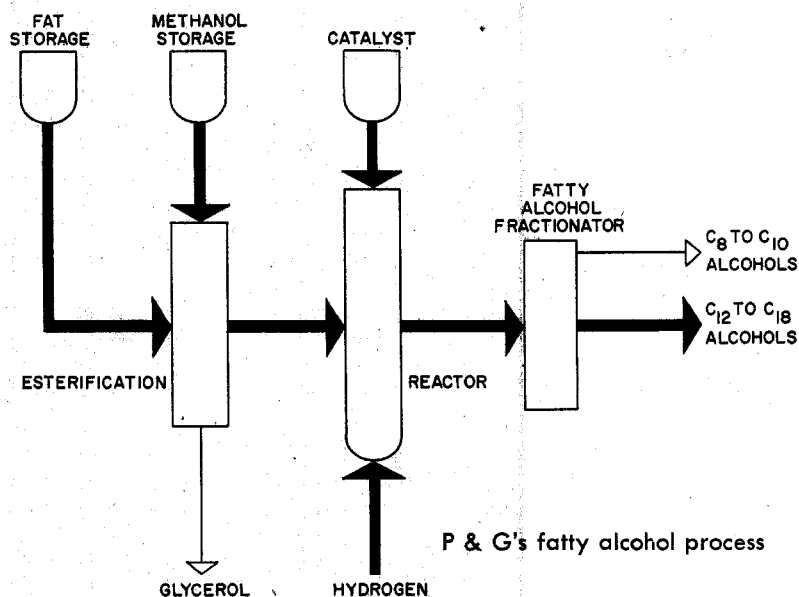
P & G's alkylbenzene suppliers can make this detergent raw material through several routes. However, they have the following (8) in common:

► Prepare an alkyl side-chain component which may be an olefin or an alkyl halide. Chlorinated kerosine has some commercial use for this purpose today but polymerized propylene is without doubt the most widely used side-chain component now.

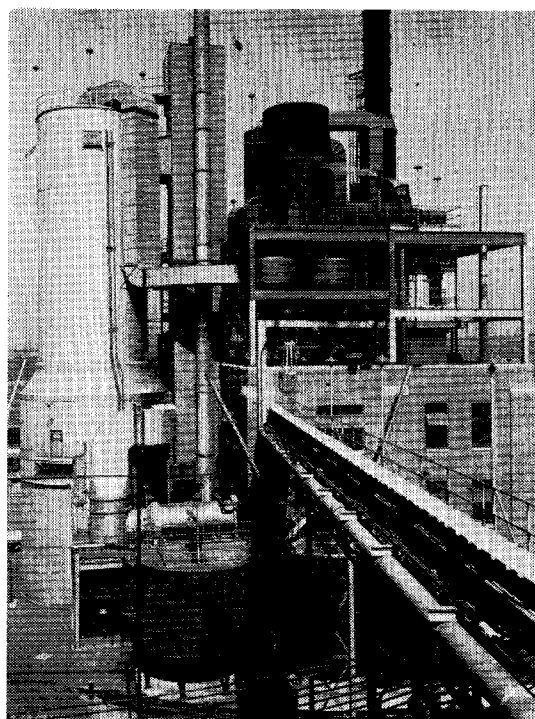
► Condense with benzene in a Friedel-Crafts type reaction, using any one of several available catalysts: HF , BF_3 , $AlCl_3$, H_2SO_4 , H_3PO_4 . With olefins, anhydrous HF is apparently the most popular.

From the delay step, the intermediate goes to a neutralizing system for conversion to the sodium salt. The time elapsed from start to this step is about 5 minutes.

The neutralizer system is also a "dominant bath." It consists of a neutralizer, surge tank, a large heat exchanger, and a caustic mix pump. The amount of caustic added (varies in strength from 50 to 70%) is controlled by an automatic pH controller. The neutralized slurry circulates around the loop at a rate of 20 volumes moving to one volume added. Mixing takes place at two points: in the neutralizer and at the caustic mix pump.



P & G's fatty alcohol process



Port Ivory, Staten Island, N. Y., detergent plant

At the caustic mix pump, freshly added caustic mixes with already circulating neutralized slurry. In turn, this slurry is pumped to the neutralizer where it is mixed with freshly added intermediate. Revolving shear plates help bring about more intimate mixing.

From the neutralizer the slurry formed

P & G Has Excellent Safety Record

Last year P & G set an enviable safety record—only 1.32 injuries per million man-hours worked, compared to an all-chemical industry average of 3.28. Two reasons are behind this record. The company:

- Engineers safety into every process.
- Makes sure all employees follow safe practices in every operation.

The policy of engineering safety into a process applies to the sulfation process. For example, a special self-priming pump is used for oleum unloading rather than compressed air. This prevents SO_3 from escaping into the area. Face shields and rubber protective clothing must be worn by the unloader.

Face shields or safety goggles are also worn by everyone in the processing area. Special thermally sensitive relief valves are used in the sulfation dominant bath system to relieve pressures which may result from overheating in the closed system.

passes to a surge tank and through large heat exchangers to remove the heat of neutralization (1000 B.t.u. per pound of alkylbenzene). From the cooler, the slurry cycles back to the caustic mix pump, completing the neutralizing bath.

Sulfation Variation

The same equipment is used to make alkyl sulfates as is used to make sulfonates. Oleum and feed volumes are essentially the same, as are process flow rates and material circulation ratios.

However, in sulfating, the object is to get the sulfate intermediate into neutralization as quickly as is possible to prevent side reactions. Time is critical and the delay step is much shorter. Also, process temperatures are held below 130°F . to deter side reactions. Only a few minutes elapse between initial reaction and the time for the intermediate to get to the neutralizer. From this point the process steps are identical with those used in making sulfonates.

Sulfonates and Sulfates

At times, P & G makes mixed sulfonate-sulfate detergents, in what the company calls "series sulfation." This is done by joining together two units—one for the sulfonation step, the other for the sulfation part. Again, process details are the same as for the respective sulfonation and sulfation reactions. But the important step is to pump the sulfonation reaction mixture into the sulfation reaction mixture. Both are then cycled in the sulfation dominant bath and passed on to neutralization. The upshot of this variation is a decrease in residence time for the sulfation mix. This allows use of higher spent acid concentrations and thus results in a higher yield.

Layered Sulfonates

The final variation of P & G's fourfold unit is making layered sulfonates. Again, the sulfonation method and rates are unchanged until just before neutralization.

Then the sulfonate intermediate is diluted with water in another dominant-bath system. From here the mix is pumped through a glass-lined settling tank to allow the excess sulfuric acid phase to separate from the sulfonic acid. Adequate separation occurs in about 30 minutes.

Then the organic acid phase is pumped to neutralization for further processing. The sulfuric acid layer is removed to storage and is later sold.

On to Detergents

From neutralization the respective sulfates, sulfonates, or variation slurries are pumped to a "crutcher" where they are blended with other ingredients to meet P & G's various product formulas.

Most Maintenance on Weekends

As sulfation and sulfonation processes are continuous, most of the major mechanical maintenance work is done during the week-end shutdown. Pump packing glands and instruments are checked, and, if necessary, repaired at this time.

Because the sulfonic acids are corrosive liquids, the sulfonator and neutralizer are dismantled periodically and checked for corrosion. Tight limits are maintained on the sulfonator pump impeller clearances. Also, the neutralizer is checked closely.

P & G keeps a maintenance manual for each unit. It outlines methods to maintain equipment in top condition. Responsibility for equipment maintenance rests with a mechanical craft manager, who, along with the department manager, schedules repair work.

Here sodium tripolyphosphate, sodium silicate, optical bleaches, and other minor ingredients are added to the crutcher through a semiautomatic weighing system.

After thorough mixing, the detergent slurry is dropped to a surge tank below the crutcher and is pumped by low and high pressure pumps in series to the top of a spray dryer where the slurry is atomized into the dryer through multiple nozzles. Hot air at 400° to 500°F . moves counter to the slurry flow, and dries the detergent as it descends the tower.

A conveyor belt removes the detergent and transfers it to packaging lines where it is automatically boxed and sent to storage to await shipment to market.

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