The Use of Fatty Acids and Their Soaps in the Manufacture of Butadiene Synthetic Rubber*

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MOST people are not aware that the manufacture of soap has a direct bearing on the production of synthetic rubber, yet GR-S, the general purpose American synthetic rubber, contains 6% of fatty acid derived from the soap used in the manufacturing operation. For instance, when 800,000 tons of GR-S is produced, as was the case in 1945 and will probably be the case in 1946, there is required about 125,000,000 pounds of soap or 7% of the total amount made in this country. Moreover, the soap that is used must be of the highest quality and must meet a rigid set of specifications. Both the quantity used and the quality of the soap are determined, not by any whim of the manufacturer of the synthetic rubber, but rather by precise physical and chemical conditions that must be met in the manufacturing process.

First let us investigate what a synthetic rubber actually is and how it is made. A rubber may be pictured as a tangle of ultra microscopic molecules several thousand times as long as their cross sectional diameter. In synthetic rubber these molecules are formed by polymerization, that is, by a process in which small simple molecules are joined together end to end much like links in a chain. This process of polymerization can occur, for example, when a liquid composed entirely of these simple molecules is treated with a catalyst that causes the polymerization process. This is known as mass polymerization since there is secured a block or mass of rubber (which however is hard to remove from the container). Moreover, the product is so viscous that it is practically impossible to stir it during the process, hence removal of the heat of polymerization is a serious problem. This process does not require soap and has not been used to any great extent for making synthetic rubber in this country. Nevertheless, it was used by the Germans who made certain special rubbers such as Buna 85 or Buna 32 by this process.

An obvious improvement in the mass polymerization process would be to dissolve the monomer in an inert solvent so as to maintain lower viscosity and thus afford an opportunity for the removal of heat during polymerization. This process again requires no soap, nevertheless for it to operate economically tremendous quantities of solvent must be recovered and reused. This process has been used in this country for the manufacture of GR-I, or Butyl, the synthetic rubber used to a considerable extent in the manufacture of inner tubes.

However, a third possibility can be pictured, namely, emulsification of the monomer in an immiscible liquid such as water, followed by polymerization to give a latex composed of fine particles of rubber suspended in the liquid. This process avoids difficulty due to high viscosity, for the latex maintains essentially the viscosity of the water phase. Heat of polymerization can thus be easily removed, and there is no solvent recovery problem. This process requires an emulsifying agent such as soap and is the method by which the majority of American synthetic rubber is manufactured. When the monomer used is chloroprene, the rubber formed is known as GR-M or Neoprene. When the two monomers, butadiene and acrylonitrile, are polymerized together, there is formed a *nitrile* rubber known as GR-A, Perbunan, Chemigum, Butaprene, or Hycar OR. When, however, butadiene and styrene are polymerized together the product is known as GR-S or American rubber.

The Function of Soap in Emulsion Polymerization

In emulsion polymerization both the water and the soap perform very definite functions. Most of the evidence supports the theory that polymer particles originate by the polymerization of monomer molecules dissolved in the aqueous phase or solubilized by the soap present. Polymer growth then continues at interfaces where soap is concentrated, in micelles or on the surface of polymer particles. The following experiment shows simply initiation of polymerization in the water phase and not in the monomer phase. Thus, if a layer of acrylonitrile is poured into a tube over a 6% solution of potassium persulfate and allowed to stand at room temperature without agitation, the water layer soon becomes cloudy due to the formation of finely dispersed polymer. The interface between the two liquid layers remains perfectly clear as does also a zone of about 5 mm. below the interface. Apparently acrylonitrile diffusing into the aqueous phase to replenish that removed by polymerization has had insufficient time to undergo polymerization during its diffusion through the upper portion of the aqueous phase (1).

Another fact indicating that initiation of polymerization occurs in or adjacent to the water phase is the observation that water soluble initiators such as hydrogen peroxide, potassium persulfate or diazonium salts in the usual polymerization systems are much more effective initiators of emulsion polymerization than oil soluble materials such as benzoyl peroxide.

Soaps exert a profound effect upon the initiation and speed of polymerization, their efficiency being roughly in the same order as their solubilizing action (2) for the monomers (3). Thus there are many synthetic detergents more efficient than fatty acids for emulsifying the monomers yet of small value in initiating polymerization. Methyl cellulose (3) and other non-ionic emulsifying agents fall in this class.

The amount of monomer solubilized by a soap is always less than the weight of the agent causing this action, yet the total amount solubilized is roughly proportional to the soap content (3). In emulsion

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polymerization the rate of polymerization is roughly proportional to the concentration of fatty soap. Thus as shown by Harkins, Heller, *et al.* (4) the amount of GR-S polymer formed from butadiene and styrene in six hours at 50°C., is as follows:

Concentration of soap in aqueous phase	0	1%	2%	3%	5%	7%
Conversion of monomers to polymer	Very small	10%	24%	34%	59%	76%

These two observations in conjunction afford evidence therefore that, other things being equal, the rate of polymerization is proportional to the solubilization of the monomers.

The soap therefore performs a much more basic function than merely emulsifying the monomer—it participates in the initiation of the polymerization and influences the emulsification of the resultant polymer. Thus if *vapor* of monomer is supplied to a solution of fatty acid soap even in the absence of agitation, polymerization and formation of an emulsion of polymer occurs. In this case, initiation of polymerization is a homogeneous process and cannot be attributed to activity at an interface between liquid monomer and soap solution (1) since here there is no such interface.

Further if a fatty acid soap solution containing polymerization catalyst is carefully introduced below a layer of monomer and allowed to stand without agitation, polymerization occurs and the water layer becomes milky due to the formation of emulsified polymer in the water phase. Agitation and pre-emulsification therefore are not responsible for the formation of this emulsion.

In the absence of agitation, rate of diffusion of the monomer may be a limiting factor in the rate of polymerization. Agitation therefore is important because it breaks up the monomer thereby furnishing a greater interface for the diffusion process. However, in a stirred reactor even comparatively inefficient stirring may be sufficient to assure a maximum rate of polymerization and emulsification of polymer, more rapid stirring and better emulsification of monomer in this case having no effect upon the rate of polymerization. Pre-emulsification of the monomers in the soap solution in such cases would obviously be expected to have little effect upon the speed of polymerization.

The progress of emulsion polymerization may be summarized as follows including a number of concepts published by Harkins (5). Polymerization of monomers starts in the micelles of soap which in turn are rapidly depleted during the course of the polymerization since the polymer particles as formed adsorb a layer of soap from the water layer which in turn causes solution of the micelles. When a mass of polymer equal to roughly two to three times the mass of the soap has been formed, no micelles are left in the aqueous phase. There are then relatively few new particles formed, and polymerization continues on the polymer particles already present, causing an increase in their size. Monomer dissolves in and swells these particles so that long before polymerization is complete there are no droplets of emulsified monomer remaining. At the end of the polymerization there is relatively little soap left in the water phase, so little as a matter of fact that the latex will scarcely foam. There is shown by surface tension measurements (6):

	Surface tension as measured in dynes/cm. at 28°C.*
Water used	74
0.1% soap solution	32
GR-S latex when 75% of monomers are polymerized	65-67

* By Du Noüy Tensiometer—uncorrected.

Long before the completion of polymerization, due to depletion of soap in the equeous phase the particles of polymer are only partially covered with soap, thus leaving an unsaturated surface. Latex of this type may be stabilized by adding more soap or some other surface active material to saturate the surface. In the usual manufacturing process it is not necessary to stabilize the particles since the latex is to be processed immediately for solid rubber.

The coagulation of synthetic rubber latex is quite similar to the coagulation of any soap stabilized emulsion. Addition of dilute acid or aluminum salt causes coagulation of the particles and conversion of the soap to fatty acid or aluminum soap. The curd so formed contains all of the fatty acid originally present in the soap. Since fatty acid is a common compounding ingredient normally used with GR-S, it is not extracted but left with the rubber. In some of the *nitrile* rubbers fatty acid would be an undesirable ingredient hence after coagulation the fatty acid is reconverted to soap with dilute alkali and washed from the crumbs. In either case the crumbs are washed with water, dried and compressed into sheets or bales for commercial use.

Soaps have a remarkable and essential action in emulsion polymerization. Since *fatty acid* soaps are common and relatively cheap, they were used first in the manufacture of American synthetic rubber. However, there are some disadvantages associated with the use of fatty acid soaps—GR-S containing fatty acid is not as tacky as might be desired and certain finished articles made from it have undesirable properties that might be avoided if fatty acid were absent. To meet these needs GR-S has been made using the sodium salt of specially purified disproportionated rosin acid (7, 8). This synthetic rubber known as GR-S-10 imparts greater tack to unvulcanized rubber stocks made from it and thus makes building and assembling operations easier. The vulcanized rubber products also show appreciably better service properties (9).

Specialty synthetic rubbers with other desirable characteristics can be made using certain cationic emulsifying agents. Salts of dodecyl amine and of diethylaminoethyl oleamide for instance can be used. Both of these materials start with fatty acids in their preparation.

Certain sulfonate dispersing agents such as the higher alkyl benzene sulfonates and condensed alkyl naphthalene sulfonates have shown value when used in small amounts for they stabilize the latex and prevent build-up of deposits in the reactors and on the containers.

Value of Specific Soaps of Fatty Acids

Now that the function of soap in emulsion polymerization has been described, let us compare specifically the different types of soaps and the effect of composition and purity.

In order to obtain uniform results the soaps must be pure and clean. Freedom from "dirt" is, of course, important. However, there are a number of specific impurities that may be much more harmful than "dirt," i.e., undissolved non-soap materials. Foremost among these must be mentioned contamination with metallic salts or soaps such as those of iron, copper, or manganese. While the amount that can be tolerated for storage stability and for threshold of inhibition of polymerization varies considerably, nevertheless the specification limits for iron (30 p.p.m.), copper (10 p.p.m.), and manganese (2 p.p.m.) have proved to be satisfactory in practice (10).

Inhibitors are present in certain fats and oils. These cause difficulty by giving slow and variable rates of polymerization. To be avoided are both natural inhibitors and synthetic ones such as alpha-naphthol which are occasionally present or added to retard rancidifying of the oil or fat.

A wide range of fatty acids can be utilized for making soaps for use in the emulsion polymerization process. If sodium soaps of the specific pure acids are investigated, it is found that the lowest member that gives a reasonable rate of polymerization is sodium undecylate. The comparative value of the sodium soaps of the common specific fatty acids in making GR-S at 50°C. is shown in the following table (11):

Sodium soap of:	Percentage conversion of Monomers to Polymer in 12 hrs. at 50°C.
Lauric acid	71
Myristic acid	75
Palmitic acid	83
Stearic acid	82
Oleic acid	82
Elaidic acid	81
Palmitic acid 90% Linoleic acid 10%	72
Palmitic acid 90% Linolenic acid 10%	41
USP "Oleic acid"	Variable—40-60
Mixed hydrogenated tallow acids	80

It should be noted that in this case the activity holds up well with the higher acids, being satisfactory even with arachidic and behenic acid soaps.

In the preparation of nitrile rubber at 30°C. (12) the peak is at the myristate, activity falling off appreciably with the higher soaps.

Sodium soap of:	Rate of Polymerization
Lauric acid	Good
Myristic acid	Excellent
Palmitic acid	Good
Stearic acid	Fair
Oleic acid	Excellent
Linoleic acid	Inactive
Linolenic acid	Inactive
Mixture of palmitic, stearic, oleic acids	Excellent
Mixture of palmitic, stearic, linoleic acids	Poor

Special attention should be directed to the harmful effect of linoleic, linolenic, and other highly unsaturated non-conjugated acids if present in soaps to be used in emulsion polymerization. The harmful effect has been shown quantitatively by Pfau and Wilson (10). In the polymerization of GR-S at 50°C. each 1% of the poly-unsaturated acid present causes a decrease in yield at the end of 12 hours as follows:

For linoleic acid	1.4%
For linolenic acid	4.5%

Methods for estimating polyunsaturation therefore are extremely important in maintaining quality and uniformity. The difference between iodine number and thiocyanogen number has been used as a measure of polyunsaturation. However, by use of an ultraviolet spectrophotometer it is possible to determine rapidly not only the extent but the kind of polyunsaturation. This instrument is now used for production control of hydrogenation and also to check purchase specifications set up to insure uniform high activity of the soap used in making GR-S (13).

As might be expected based on the micellar action of the soaps, the lower members are more satisfactory for polymerization to be run at lower temperatures while the higher members show better solubility and activity at the higher temperatures. The trend is definitely toward polymerization at lower temperatures for the majority of the evidence shows that in any given recipe the lower the temperature at which the polymerization is performed, the higher the quality of the rubber. This would indicate a future trend toward soaps with high myristic acid or recrystallized oleic acid content or wider use of the more soluble potassium soaps.

In certain hydrogen peroxide initiated polymerizations such as are used in the manufacture of nitrile rubber, superfatting of the soap has a profound effect upon the speed of polymerization. This is shown in Figure 1 in a nitrile rubber polymerization run at 30°C. (14).

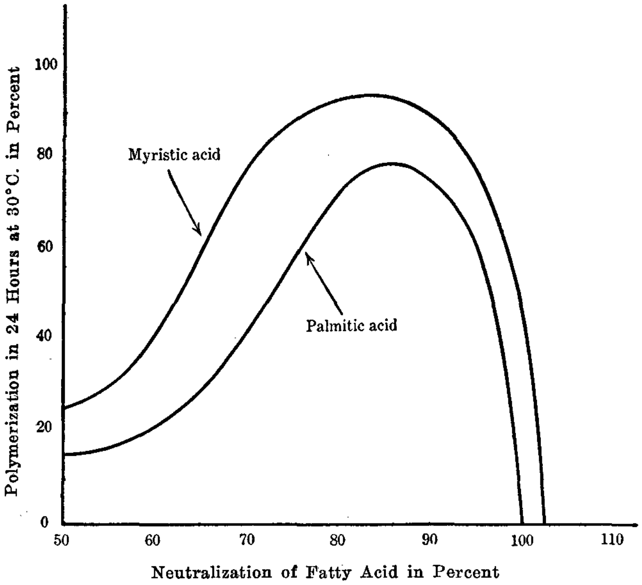

FIG. 1. Effect of degree of neutralization upon conversion of hydrogen peroxide initiated nitrile rubber.

Obviously when such a polymerization is performed from 10 to 15% of the fatty acid in the soap should not be saponified. This result can be obtained either by adding fatty acid to the neutral soap or by adding a strong acid such as sulfuric to the soap solution to set free some of the fatty acid. On the other hand an excess of alkali in the soap yields more stable latices. Recently polymerization recipes have been developed such that rapid polymerization can be obtained even in the presence of as much as a 10% excess of alkali.

Special recipes for making emulsion polymers have also been developed for use where high grade fatty acids are not available. Thus, as a result of their shortage of fats and oils during the war, the Germans used a linseed oil soap in the manufacture of Buna. This actually served a real function yet it did greatly slow down their production. Later when even this became unavailable they used synthetic fatty acid prepared by the oxidation of Fischer Tropsch paraffin.

Research work in this country has shown that synthetic rubber can be made from polyunsaturated acids and other low grade fatty acids at present production rates if special activators are used to compensate for the inhibiting effects. However, these types of rubber have never been tested extensively on a commercial scale and do introduce a number of new difficulties into the manufacturing operations.

Trends in the Manufacture of Soaps for Use in Making Synthetic Rubber

There has been a noticeable trend in the fatty acids or soaps used in the manufacture of synthetic rubber. At first distilled myristic and palmitic acid from spermaceti was used. This was replaced soon by distilled myristic acid from coconut fatty acids. When the supply of this became short, soap made from selectively hydrogenated tallows and greases was used. Large scale manufacture of GR-S necessitated larger quantities of soap. This was obtained first from high grade edible tallow and finally from hydrogenated oils, tallows, and greases.

Future developments point to the use of highly purified fatty acids or soaps having a definite ratio of the various fatty acids present. Crystallized acids are quite satisfactory and uniform in their activity. For example, crystalline palmitic acid would be desirable in certain cases while for others a crystallized high purity oleic acid free from polyunsaturates would be ideal. Improvement in crystallization processes and development of markets for the polyunsaturated acids obtained as by-products will help to bring these things to pass. Proper economic analysis of the technological progress in the related fields will certainly determine the course of the future in this field.

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The Hydrolysis of Fatty Acid Chlorides

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IN the course of the preparation of a series of synthetic glycerides of known molecular configuration it was necessary to store the acid chloride (1) intermediates for various periods of time. The freshly distilled acid chlorides were stored in sealed glass ampoules and analyzed prior to use. After several months of storage under these conditions no appreciable hydrolysis could be detected. It was realized, however, that under commercial conditions of storage more or less hydrolysis might occur from the presence of moisture, and it appeared advisable, therefore, to determine the relative rates of decomposition of the more commonly used saturated and unsaturated fatty acid chlorides.

A search of the literature revealed little information on the relative rates of hydrolysis of acid halides. Velasco and co-workers (4, 6) investigated the velocities of hydrolysis of acetyl chloride, chloroacetyl chloride, propionyl chloride, and butyryl chloride. The degree of hydrolysis was determined by measuring the extent of diffusion of the reaction products into water and toluene at 25° C. and 45° C. These investigators reported that hydrogen ions do not catalyze any of the hydrolytic reactions of the chlorides, which would indicate that the mechanism of hydrolysis in this case is different from that of the esters and amides of the fatty acids. Similar results have been reported by Velasco and Ollero (5) and by Karvé and Dolé (2, 3) with respect to the rates of hydrolysis of a number of aromatic acid chlorides. The acid halides used by the latter investigators were dissolved in chloroform or benzene and shaken with water at a constant rate. Hydrolysis was found to occur at the boundary between the two liquid phases at rates which were determined by diffusion of the reactants and reaction products across the interfacial boundary. The rate constants were found to increase with increasing concentration of acid halide. The hydrochloric acid formed during hydrolysis was found to exert no catalytic action. Conical flasks were said to favor the hydrolysis.

Since there are no available data on the hydrolysis of the higher fatty acid chlorides, experiments were made to determine the hydrolysis of a number of saturated and unsaturated fatty acid chlorides when shaken with water for varying periods of time.

Experimental

Purification of the Fatty Acids and Preparation of Fatty Acid Chlorides. The saturated and unsaturated fatty acids, with the exception of octanoic and decanoic, were purified by the method described by Bauer (1). Commercial preparations of octanoic and

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