# Effect of Preemulsifying Mercaptans on Modification in Emulsion Polymerization Systems

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## Synopsis

Preemulsifying modifiers, or their solutions in monomers, with soap and water prior to charging the remaining ingredients of an emulsion polymerization system markedly changes the reactivity of high molecular weight modifiers. The increased reactivity of a mercaptan is seen in a higher regulating index as measured by the rate of depletion of the mercaptan. The regulating index of *tert*-hexadecyl mercaptan for a styrene-butadiene copolymerization (SBR) increased from 0.3 for the control to 3.0 after preagitation, and thus approached the *tert*-dodecyl mercaptan control in efficiency on a molar basis. The regulating index of *n*-dodecyl mercaptan increased from 1.0 for the control to 16 for the experimental. The latter value is too high for efficient modification of SBR systems. This technique permits the attainment of a continuous range of regulating index values within limits based on the reactivity of the modifier and intensity and duration of preagitation. This paper presents solutions for two of the problems associated with the preagitation technique and proposes a mechanism to account for the changes in modification arising from preagitating modifiers in the soap solution. This report develops a variable in emulsion polymerization that has been little used and incompletely understood.

## INTRODUCTION

The original objective of this research was to devise a procedure for using high molecular weight mercaptans efficiently as modifiers in emulsion polymerization systems as a means of reducing odor in these latices and products. Mercaptans heavier than dodecyl are relatively inefficient modifiers in SBR systems because of their low rates of depletion. *tert*-Hexadecyl mercaptan, for example, has a regulating index of 0.3 in an SBR 1500 formulation, and 3.4 parts are needed to produce a 50 Mooney viscosity polymer.

Some of the early workers in emulsion polymerization showed that increasing agitation during the course of polymerization increased the rate of depletion of mercaptan in SBR type of recipes.[1-3] The increased rate of depletion was attributed to the increased transport of mercaptan between phases arising from the greater surface of the smaller emulsion particles formed by the more vigorous agitation.

Little work, however, was done on preagitating the mercaptan and soap solution prior to charging the other ingredients. An in situ technique involving the formation of soap in presence of monomers and mercaptan

prior to charging the remaining ingredients of a recipe has been reported.[4]
Preagitating all the ingredients of a recipe, except for the initiator system,
for a long time in a laboratory bath before initiation greatly improved the
modification with *tert*-hexadecyl mercaptan.[5] Almost all reviews of
emulsion polymerization either omit or only briefly mention the influence
of preagitation on emulsion polymerization systems.

The incentive of finding a means of utilizing high molecular weight
mercaptans led us to the investigation of the preagitation technique, and as
the results evolved, the study was broadened to include standard modifiers
used in the SBR industry.

## EXPERIMENTAL PROCEDURES

### Materials

The commercial tertiary mercaptans, Sulfole 120, 132, and 160, have
been previously described.[6,7] The normal dodecyl mercaptan used in
part of this study is a new development mercaptan available from Phillips
Petroleum Company. The monomers, emulsifiers, and initiating in-
gredients are all commercial-grade products used in standard SBR poly-
merization.

### Polymerization Recipes

The standard SBR 1500 and 1503 formulations were used throughout this
study,[8,9] and polymerizations were conducted by the bottle technique.[10]
In the majority of the exploratory experiments with Sulfole 160 mercaptan,
0.5 parts per hundred of monomers (phm) was used.

### Preagitation

Three procedures were employed during the course of this study. The
first consisted of rotating in the polymerization bath the aqueous phase and
mercaptan, or mercaptan–monomer solution, in a bottle for 24 hr or longer.
This technique was used originally to confirm the results of Rothlisberger[5]
and was then replaced by more efficient agitation methods.

The second procedure consisted of exposing the solutions in bottle or
metal containers to ultrasonic irradiations. The apparatus was a Model
G140-25 National Ultrasonic Corp. generator with bath for cleaning and
was used at an elevated temperature. Bottles could not be used for long
exposure to the irradiation because etching occurred and the basic solutions
were contaminated with silicate. Uncontaminated emulsions were formed
in stainless steel vessels even when irradiated for several hours. This
technique was dropped in favor of the third and most efficient procedure
used in most of.this study.

The most convenient apparatus for the preagitation was an explosion-
proof Waring Blendor, Model EP-1, provided with a stainless steel, one-
liter container with a screw-on lid. The agitation was rated at 11,000 rpm

with 32 oz of water in the container when new. The center of the lid had an $1/8$-in.-nipple and an $1/4$-in.-tubing fitting. This arrangement permitted the sealing of the hole in the nipple with a rubber gasket through which all solutions and gases could be injected or expelled by use of the syringe technique. By this means all transfers and agitation could be done under a controlled atmosphere. In most of the preagitation experiments, the entire aqueous phase was agitated with all the modifier or the modifier dissolved in the monomers. The pH of the soap solution before agitation was adjusted to 10.5–10.8 and, if necessary, again before charging.

With 300 ml of soap solution in the Waring container, a temperature of 65°C would be reached in 10 min at the highest rotor speed. A temperature of 100°C would be reached in 20 min when an air blast would be used to maintain this temperature. A Cambridge surface thermometer was used to measure the temperature.

## Soap Solution Preparation

The soap, auxiliary emulsifier, electrolyte, and base were added to hot distilled water which had been preboiled at least 10 min. Boiling in an open beaker was continued at least 5 min while pH was adjusted to 10.5–10.8. The solution was transferred to a bottle and handled out of contact with air from this point on by the syringe technique until polymerization was completed. In instances when the soap solution was pretreated, 0.1 g sodium dithionite per 4.6 g soap was added to the water phase before boiling was started.

## Charging Procedure

The emulsion from the Waring container was pressured into a sealed polymerization bottle and the remaining ingredients, with initiator system withheld, were added by syringe, except butadiene which was charged in the usual manner. The bottle was then rotated in the polymerization bath for $1/2$ hr before initiation.

## Mercaptan Analysis

The Kolthoff-Harris amperometric-silver nitrate procedure was used for analyzing the mercaptan in soap solution and in latex.[11] Mercaptan content was determined after the preagitation step, and mercaptan depletions during polymerization were measured from this point. This handling of data reflected the effective modification better than would the normalized treatment of only the data for the polymerization portion of the experiment. The regulating index, $r$, is defined as $r = d(\ln S)/dx$. The value of $r$ is obtained by plotting $\ln S$ versus $x$, and the slope gives the value of $r$; $S$ and $x$ are the per cent modifier remaining and the fractional conversion. In Figures 2, 4, 5, and 6, only the linear portion of the curve was used to calculate the regulating index.

## Peroxide Analysis

Peroxide in some fatty acids and soaps was determined by an ampero-metric application of the iodide procedure of Wagner and associates.[12]

## Molecular Weight Distribution

The Waters' gel permeation procedure and means of handling the data in this laboratory were previously reported.[13]

## EXPERIMENTAL RESULTS

The effectiveness of the three methods of preagitating, end-over-end in a polymerization bath, ultrasonic irradiation, and high-speed Waring Blendor, on Mooney viscosity is shown in Figure 1. The curves in Figure 1 show the marked improvement in modification obtained by all three techniques, and that duration was greatly reduced as the intensity of agitation was increased. The curves exhibit a tendency for the Mooney to level out as the agitation time is increased. As was mentioned in the experimental section, the less effective techniques were abandoned in favor of the Waring Blendor.
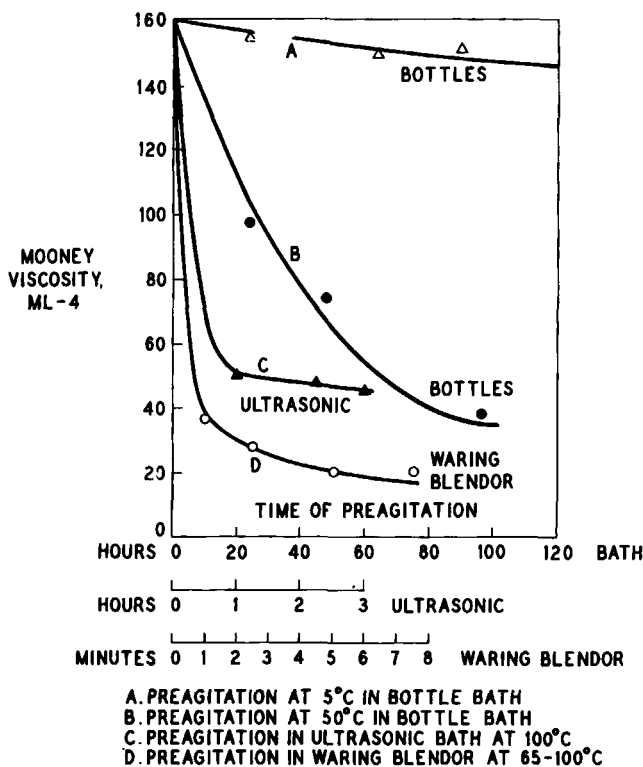


A. PREAGITATION AT 5°C IN BOTTLE BATH
B. PREAGITATION AT 50°C IN BOTTLE BATH
C. PREAGITATION IN ULTRASONIC BATH AT 100°C
D. PREAGITATION IN WARING BLENDOR AT 65-100°C

Fig. 1. Effect on Mooney viscosity of time of preagitation by different agitation methods. All polymerizations SBR 1500 type with 0.5 phm $t$-$C_{16}$ SH.

## Problems Associated with Preagitation

Two of the problems encountered when emulsifiers and mercaptan are preagitated in the Waring Blendor are shown by the mercaptan depletion curves and data in Figure 2. With potassium oleate, stearate, and laurate, 28%, 17%, and 6%, respectively, of the mercaptan was lost during the 40-min preagitation period in the Blendor, but only several per cent disappeared in the rosin soap solution. With potassium oleate and stearate and to a lesser extent with rosinate, an abnormal depletion of mercaptan is seen during the first 10% of conversion. After this abnormal depletion, the disappearance of mercaptan seems normal as shown by the linear portion of the curves. The resultant effect of the loss of mercaptan during preagitation, the abnormal depletion, and the normal depletion is seen in the viscosity data of the polymers, Figure 2. For the stearate and oleate systems, the loss of mercaptans in side reactions is too great to overcome the benefits from the improved regulating index. Although the loss of mercaptan is low in the laurate system, the regulating index is too low for efficient utilization of the modifier. Rosin soap gave the most favorable result.

Peroxides were suspected as being the cause of the loss of mercaptan during the preagitation step. Active oxygen was determined for some fatty
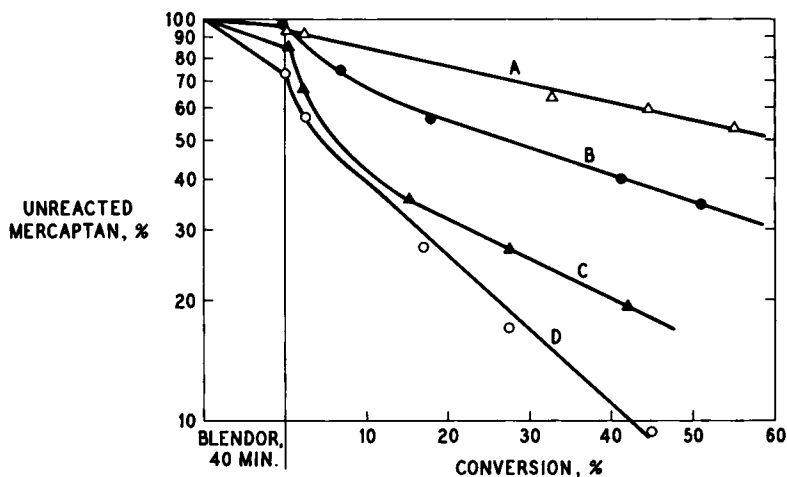


Fig. 2. Loss of $t$-$C_{16}$ SH during preagitation and depletion during polymerization with different soaps in an SBR 1503 type system:

| Curve | Soap | Regulating index | Viscosity | |
| | | | $\eta_{inh}$ | ML-4 |
|---|---|---|---|---|
| A | K laurate | 1.1 | 3.68 | 153 |
| B | K rosinate | 1.5 | 1.98 | 50 |
| C | K stearate[a] | 2.3 | 3.25 | 110 |
| D | K oleate | 4.4 | 2.95 | 89 |

[a] Made from Emersol 132 stearic acid.

TABLE I

Active Oxygen Contents of Fatty Acids and
Soaps Used in Emulsion Polymerizations

| Fatty acid or soap | Active oxygen, % |
|---|---|
| Lauric acid | <0.0001 |
| Stearic acid, Emersol 132 | 0.0004 |
| Potassium soap chips, Swift and Co. | 0.0006 |
| SF Flakes (sodium stearate) | 0.0032 |
| Dresinate 554 soap | 0.0037 |
| Stearic acid, Procter and Gamble | 0.035 |
| Oxidized P and G fatty acid[a] | 0.153 |

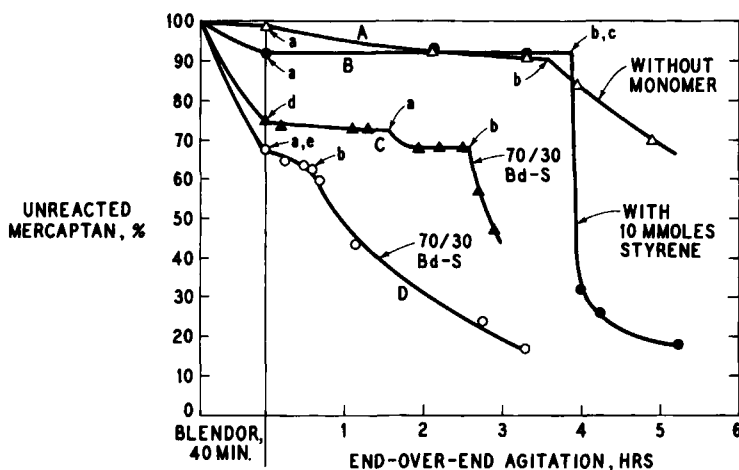[a] Procter and Gamble fatty acid heated in air oven for 105 hr at 68°C.



Fig. 3. Effect of active olefins on depletion of $t$-$C_{16}SH$ in presence of free radicals. (A) K stearate-$t$-$C_{16}$ SH preagitated 40 min in Blendor, PMHP at a and activator at b. (B) K stearate-$t$-$C_{16}$ SH preagitated 40 min in Blendor, PMHP at a, activator and 10 mmole styrene at b, c.   (C) K oleate-$t$-$C_{16}$ SH preagitated 40 min in Blendor, 70/30 butadiene-styrene at d, PMHP at a, activator at b.   (D) K stearate-$t$-$C_{16}$ SH for 40 min and 30 styrene 5 min preagitated in Blendor, PMHP and 70 butadiene at a, e, activator at b. a. 0.36 mmole $p$-menthane hydroperoxide (PMHP); b. 0.036 mmole complexed iron activator;[9] c. 10 mmole styrene; d. 70/30 butadiene-styrene; e. 70 butadiene.

acids and soaps used in emulsion polymerization,[12] Table I.   Losses of mercaptan during preagitation, seen for the soaps in Figure 2 and for potassium fatty acid soaps in Figure 3, do not correspond with the active oxygen contents.

Another factor suspected of contributing to the loss of mercaptan during preagitation was the presence of reactive unsaturation.   This was tested by preagitating potassium oleate and stearate soap solutions with Sulfole 160 mercaptan; and to a portion of the stearate emulsion, 10 millimole styrene and the normal amount of $p$-menthane hydroperoxide were added before the initiator was added to the preagitated emulsion at 5°C in absence of the monomers, Figure 3, curve B.   Curve B in Figure 3, compared with
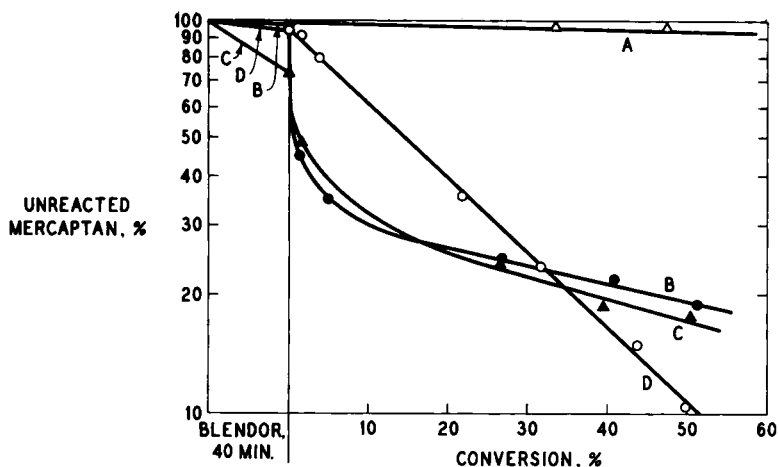
Fig. 4. Elimination of loss of mercaptan during preagitation with dithionite and elimination of abnormal depletion with styrene in a potassium fatty acid emulsified system:

| | $Na_2S_2O_4$, | Styrene, | Regulating | Viscosity | |
| Curve | phm | phm | index $r$ | $\eta_{inh}$ | ML-4 |
| --- | --- | --- | --- | --- | --- |
| A | — | — | 0.22 | 3.60 | — |
| B | 0.1 | — | 1.3E[a] | 3.53 | 130 |
| C | — | — | 1.4E[a] | 3.29 | 113 |
| D | 0.1 | 30 | 4.32 | 1.95 | 40 |

[a] Estimated from linear portion of curve.

curve A containing no unsaturates, shows the pronounced loss of mercaptan when free radicals are formed in the presence of reactive olefins. Curve C for the experiment with oleate shows the serious loss of mercaptan during preagitation, and curve D for stearate with styrene shows the serious loss of mercaptan when it is agitated with a reactive olefin.

The curves in Figure 4 show how the losses of mercaptan due to side reactions can be overcome for the standard industrial potassium fatty acid soap as the emulsifier. Curve A shows the very inefficient depletion of mercaptan in the control system. Curve C shows the loss of mercaptan during preagitation and during the first 10% of conversion. Curve B shows that the loss during the preagitation can be overcome if the soap solution is first boiled with 0.1 part sodium dithionite per 4.6 parts soap for at least 10 min before use in the preagitation step, but the loss during the initiation step still persists. Curve D shows that both the side reactions causing loss of mercaptan can be overcome if the mercaptan is dissolved in the monomer before the dithionite-treated soap emulsion is prepared in the Waring Blendor. The tabulated data show the resultant effect of the losses of mercaptan and the prevention of these losses on the viscosity of polymer prepared in the presence of 0.5 part Sulfole 160 mercaptan to 60% conversion.
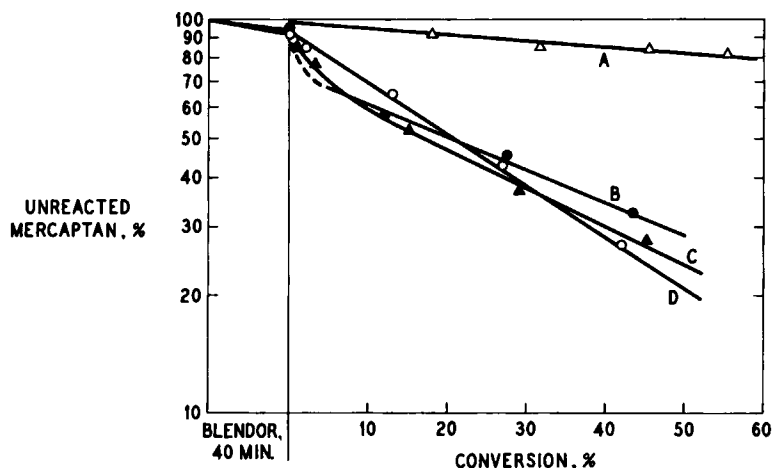
Fig. 5. Treatment of rosin soap solution with dithionite before preagitation and elimination of abnormal depletion with styrene in a potassium rosin soap emulsified system:

| Curve | $Na_2S_2O_4$, phm[a] | Styrene, phm[b] | Regulating index $r$ | Viscosity | |
|---|---|---|---|---|---|
| | | | | $\eta_{inh}$ | ML-4 |
| A | — | — | 0.3 | — | — |
| B | — | — | 1.83 | 2.01 | 50 |
| C | 0.1 | — | 2.14 | 1.98 | 57 |
| D | 0.1 | 30 | 2.96 | 1.56 | 35 |

[a] Soap solution boiled 10 min with dithionite before agitation.

[b] Styrene present during preagitation.

Figure 5 shows the same set of experiments carried out with rosin acid soap as the emulsifier. In this set of experiments, as was seen in the previous experiment with rosin soap, the loss of mercaptan during preagitation with or without pretreatment with sodium dithionite is not serious. However, preagitation of the modifier in the presence of the monomer was beneficial. In another set of experiments of pretreatment with dithionite, the boiling time had to be extended to 40 min before the loss of mercaptan during preagitation was completely eliminated.

Another side reaction that accompanied the loss of mercaptan during preagitation in the presence of monomer was polymerization. When the soap was pretreated with dithionite so that mercaptan loss during preagitation was negligible, polymerization of styrene was also negligible.

## Optimizing the Preagitation Technique

**Intensity of Agitation.** The results presented in Figure 1 established that the intensity of agitation greatly affects the time required to obtain an optimum modification with *tert*-hexadecyl mercaptan as the modifier. Other variables studied in the preagitation step follow.

TABLE II
Comparison of the Two-Step and the One-Step Preagitation
Procedures for Rosin Soap, $t$-$C_{16}$ Mercaptan and Styrene

| Agitation, min | | Regulating index $r$ | Viscosity | | Rate of polymerization, %/hr |
|---|---|---|---|---|---|
| $t$-$C_{16}$SH | Styrene | | $\eta_{inh}$ | ML-4 | |
| Two-Step Procedure | | | | | |
| 0 | 0 | 0.27 | 3.6 | 153 | 11.0 |
| 2.5 | 5 | 3.1 | 1.64 | 34 | 9.4 |
| 5 | 5 | 3.7 | 2.01 | 48 | 8.9 |
| 10 | 5 | 3.7 | 1.63 | 32 | 9.0 |
| 20 | 5 | 3.8 | 1.61 | 32 | 8.6 |
| One-Step Procedure | | | | | |
| $t$-$C_{16}$SH + styrene | | | | | |
| 1 | | 1.7 | — | 37 | 9.3 |
| 2.5 | | 2.2 | 1.45 | 29 | 7 5 |
| 5 | | 3.0 | 1.57 | 21 | 7.4 |
| 7.5 | | 2.9 | 1.42 | 21 | 7.3 |

**Temperature During Preagitation.** The preliminary exploratory experiments established that temperature during the preagitation period was important only if agitation was mild. For example, preagitating Sulfole 160 mercaptan in the polymerization bath at 50°C for 96 hr and then polymerizing at 5°C resulted in a Mooney viscosity lowering of over 100 units below that of the control, Figure 1; whereas preagitating at 5°C for 96 hr gave only an eight Mooney unit decrease. On the other hand, preagitating Sulfole 160 mercaptan for 5 min at either 65° or 100°C in the Waring Blendor made little difference in the regulating index and Mooney viscosity of the polymers for the two parallel experiments. Therefore, in the majority of the experiments in the Waring Blendor, no effort was made to control temperature except when the time of agitation exceeded 20 min, and then the temperature was held at 100°C.

**Amount of Water During Preagitation.** Decreasing the water in the soap solution reduced the regulating index, and no advantage was seen for use of a smaller water phase during preagitation in the laboratory experiments, so use of the total recipe amount of water in the preagitation step was adopted for most experiments.

**Amount of Soap During Preagitation.** Preagitating all the mercaptan with one half the amount of soap and then adding the other half in the normal manner lessened the abnormal depletion of mercaptan during the first 10% of conversion, but not to the extent seen when all the monomers were present, Figure 3. No particular advantage was found for forming the soap by the in situ procedure during preagitation as used by the Minnesota group.[1]

**Monomers Present During Preagitation.** In the original study of the elimination of the abnormal depletion of mercaptan during polymerization,

| Substitution for 30 parts Styrene[a] | Effectiveness of eliminating abnormal depletion |
| --- | --- |
| 5 Parts xylene | almost complete |
| 5 Parts styrene | less than with 30 parts |
| 5 Parts 20% solids SBR 1500 latex | almost complete |
| 1 Part Philrich 5 oil | slightly effective |
| 70 Parts butadiene | almost complete |

[a] The alternate ingredients were substituted for styrene for the preagitation step.

Figure 4, preagitation was carried out in two steps; the mercaptan was first agitated with the soap and then this emulsion was agitated with styrene for a fixed time. As the time of the first step was varied, the depletion measurements indicated that the two steps could be combined. The data showing the effect of variable time of agitation for the two-step and the one-step procedures on regulating index, Mooney viscosity, and rate of polymerization are shown in Table II. The one-step preagitation process is probably more efficient than the two-step procedure; and for both sets of results, the Mooney viscosities tend to level out after a certain minimum agitation period. The rate of polymerization decreases as preagitation time increases, but there is also a tendency for the rate to level out.

Other means of eliminating the abnormal depletion of mercaptan during the first 10% of conversion were tried, Table III. The alternate means of eliminating the abnormal depletion of mercaptan, Table III, offer no advantage in the laboratory over the use of all the styrene during the preagitation step. The latter procedure was used for most of the experiment once this knowledge was gained.

## Application of Preagitation to Other Modifiers

The curves in Figure 6 show the depletion data for the n-dodecyl mercaptan and Sulfole 120 mercaptan controls and for the same mercaptans preagitated for 5 min.

The curves A and D show why n-dodecyl mercaptan would prove to be an unsatisfactory modifier for controlling Mooney viscosity of low-temperature SBR. The regulating index increased from 1.0 for the control to 16 for the preagitated system. This response indicates polymerizations would be sensitive to variables that affect the transport of the mercaptan between phases. In contrast, the regulating index of Sulfole 120 mercaptan is near an optimum under normal agitation and the value is doubled after preagitation. At the higher depletion rate, Sulfole 120 mercaptan is less efficient than is the control, as is shown by the viscosity data in the tabulation. This mercaptan shows a lower sensitivity to variables affecting transport between phases than does the normal isomer.
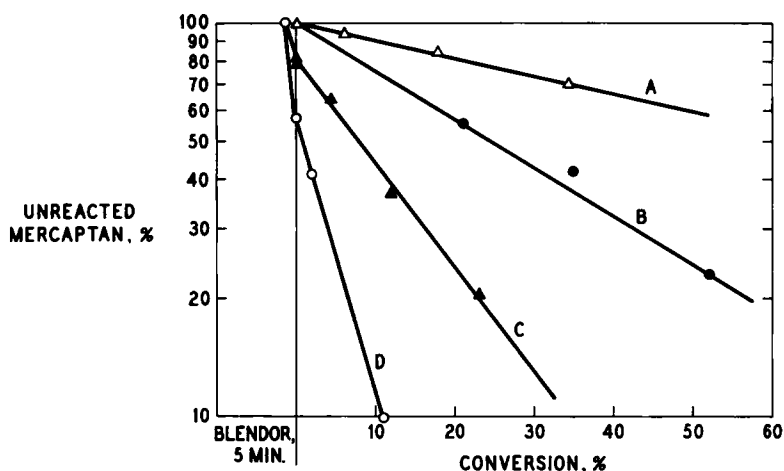
Fig. 6. Comparison of standard and five minute preagitation on modification with tertiary and normal dodecyl mercaptan in an SBR 1500 recipe:

| Curve | Charging technique | $C_{12}$ isomer[a] | Regulating index $r$ | Viscosity, $\eta_{inh}$ |
|-------|-------------------|------------|----------------------|------------------------|
| A | Standard | Normal | 1.0 | 3.18 |
| B | Standard | Tertiary | 2.8 | 1.96 |
| C | Preagitated | Tertiary | 6.1 | 2.25 |
| D | Preagitated | Normal | 16.0[b] | 3.5 |

[a] 0.2 phm.

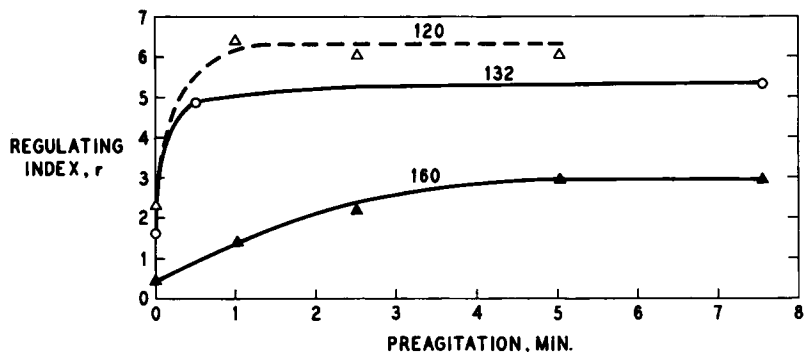[b] Estimated from linear portion as drawn.



Fig. 7. Effect of variable time of preagitating $t$-$C_{12}$, $t$-$C_{13.2}$, and $t$-$C_{16}$ mercaptans in the Waring Blendor on regulating index in the SBR 1500 recipe. The numbers refer to the commercial Sulfole mercaptans.

In the SBR 1000 recipe the regulating index of normal dodecyl mercaptan increased from 3.9 for the control to 14 for the preagitated system.

The curves in Figure 7 show how the regulating index changes with variable preagitation time for Sulfole 120, 132, and 160 mercaptans. All show a leveling off as the time of agitation increases. A much shorter time
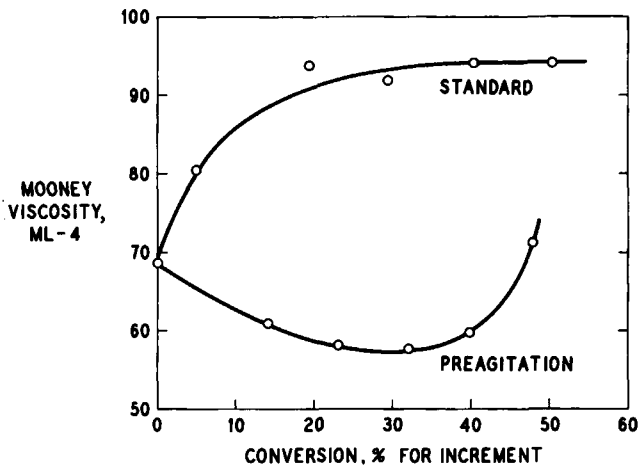
Fig. 8. Comparison of incremental addition of preagitated $t$-$C_{12}SH$ with normal incremental addition. In both experiments $^2/_3$ of the mercaptan was added initially and $^1/_3$ at the different conversions. Mercaptan and soap preagitated 20 min in Waring Blendor.

for optimum response is required for the dodecyl than for the hexadecyl mercaptan.

Previous research on the incremental addition of mercaptans in emulsion systems established that modifiers with sufficiently high regulating indexes and rates of solubilization were responsive to portionwise addition during the course of polymerization.[6] Since preagitation increased the regulating index of Sulfole 120 mercaptan, which can be attributed to an increased availability at the site of polymerization, the preagitated Sulfole 120 mercaptan-soap mixture was tested in incremental addition experiments, Figure 8. In the incremental addition experiment, the styrene was not present during the preagitation step; only soap and mercaptan were preagitated.

The curves in Figure 8 show that the preagitated Sulfole 120 mercaptan did indeed respond to incremental addition technique.

## Effect of Preagitation in the Standard Polymerization System

For the standard laboratory procedure, the entire contents of a recipe, including peroxide and mercaptan but not initiator, are preagitated end over end in the bath for 30 min, after which the initiator solution is injected. In a series of experiments, the mercaptan was added to the bottles at different times with respect to the time of initiation. This varied from 4 hr of rotation in the bath before initiation to $^1/_2$ hr after initiation. The latter time was designated as $-^1/_2$ hr of preagitation. Data relating Mooney viscosity with various preagitation time for this series of polymerization are plotted in Figure 9. This figure also includes the one point for polymer obtained after Sulfole 120 mercaptan was preagitated in the Waring Blendor for 5 min.
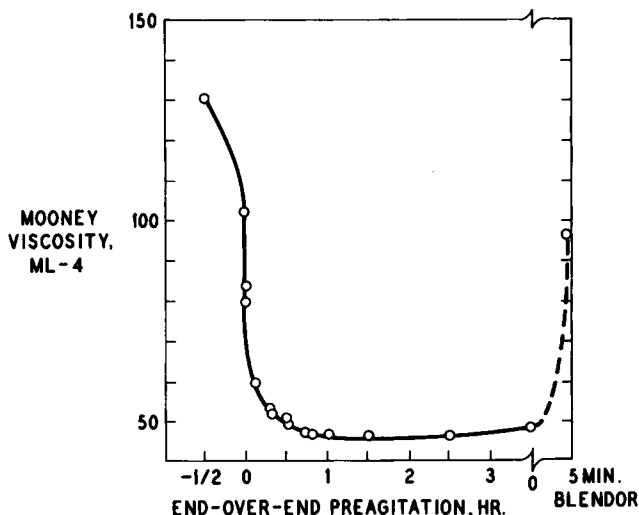
Fig. 9. Effect of duration of preemulsification of SBR 1500 recipe at 5°C: $-\frac{1}{2}$ hour means the modifier was added $\frac{1}{2}$ hour after initiation.

The curve in Figure 9 shows a certain minimum preagitation before initiation is needed for efficient modification. Short preagitation periods or addition of mercaptan after initiation can be disastrous for modification. Little advantage is gained if the preagitation is extended much beyond the minimum; and if preagitation of this modifier is too vigorous, the polymer Mooney can also be seriously affected. In the latter case, the mercaptan is consumed too rapidly for efficient modification.

## Effect of Preagitation on Molecule Weight Distribution

The molecular weight distribution and viscosity data for SBR 1500 type of polymers made with Sulfole 160 mercaptan preagitated with rosin soap and styrene by the two-step procedure in the Waring Blendor are compared with the data obtained for the polymer made with Sulfole 120 mercaptan by the control procedure to about the same viscosity in Table IV. The molecular weight distributions obtained by the preagitation

TABLE IV

Comparison of the Molecular Weight Distribution and Viscosity of Polymer Made with Preagitated Hexadecyl Mercaptan with Standard Procedure Dodecyl Mercaptan Polymer

| Mercaptan | Procedure | Amt. PHM | Regu- lating index $r$ | Viscosity | | Molecular weight[a] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $\eta_{inh}$ | ML-4 | $\bar{M}_w$ | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
| Sulfole 160 | preagitated[b] | 0.45[c] | 3.1 | 1.64 | 34 | 254 | 67 | 3.8 |
| Sulfole 120 | standard | 0.22 | 2.8 | 1.82 | 41 | 280 | 75 | 3.7 |

[a] All $\bar{M}$ are $\times 10^{-3}$.

[b] Experimental data for second polymer in Table II, this report.

[c] Mercaptan as received contained 80.1% tertiary mercaptan.

technique are as narrow as those obtained by the standard procedure with modifiers possessing the same regulating index.

## DISCUSSION

This report covers the exploratory and problem-solving phase of the research. During the course of the investigation as knowledge was gained, improved procedures evolved, but the previous experiments were not repeated to obtain better data. This has resulted in presentation of some data from experiments that are not directly comparable. But in most of these comparisons, the effects were so pronounced that a refinement of the experiment would contribute little more to the understanding of the results. With this in mind, the following discussion is presented.

### Losses of Mercaptan to Side Reactions

The original work was done with rosin acid soap, and the small losses encountered during preagitation were attributed to experimental error. However, losses found with oleic and potassium fatty acid soaps were so large that occurrence of side reactions was unquestioned. Peroxides were suspected, and their presence was found, Table I. A correlation seems to exist between loss of mercaptan during preagitation and the presence of both olefin and peroxide for all the soaps except the stearate. The reason for this exception is unknown.

Boiling the soap solution with dithionite eliminated almost all the loss of mercaptan during the preagitation step. This treatment of the soap solution also eliminated the polymerization of styrene when it was present during the preagitation step. Making the soap inert to initiation of monomers was found useful in the course of this study.

The abnormal depletion of mercaptan during the first 10% of conversion is believed to arise from a new variable introduced into the polymerization system. After preagitating this soap solution and mercaptan, the micelles should be saturated with modifiers and any remainder should be highly dispersed as an emulsion. When these micelles are exposed to monomers, they imbibe some monomer, and a small amount of the mercaptan diffuses to the monomer phase or is dissolved in the monomer phase when soap stabilizes the monomer droplets. When radicals strike the saturated micelles, the relatively high concentration of mercaptan reacts with a small amount of monomers to form monomer–polymer particles. This unfavorable depletion of mercaptan continues until the micelle phase disappears. From this point, a favorable concentration of mercaptan is in the monomer–polymer particle or on its surface, and the little mercaptan in the monomer phase is slowly transported to the site of polymerization. This is stage II of the Smith-Ewart polymerization hypothesis,[14] and the polymerization is now normal with the exception of the distribution of

mercaptan in comparison to that in a control polymerization with the same amount of modifier.

When the monomer–mercaptan mixture is preemulsified, a significantly different distribution of mercaptan exists. In this case, the micelles are saturated with the mercaptan–monomer solution and only a small amount of mercaptan is in the micelles which are the sites of initiation. The remainder of the mercaptan is in the monomer–mercaptan emulsion. These original monomer–mercaptan droplets must retain some of their identity during the remaining course of the polymerization. The reasons for this belief are given in the following section.

## Mechanism of Enhancing Depletion by Preagitation

The previous section points out that the preagitation introduces new variables into the emulsion polymerization system. Preagitating soap and mercaptan should give micelles saturated with mercaptan. Mercaptan preagitated with soaps of stearic, oleic, fatty acid, and rosin acid resulted in enhanced modification accompanied by abnormal depletion during the first 10% of polymerization, Figures 2, 4, and 5. The latter depletion should be avoided for optimum modification so the simple preagitation of mercaptan and soap is not the preferred procedure, except when an incremental addition of high molecular weight mercaptan is to be used. In the latter case, the micellar solubilized mercaptan is rapidly transported to the monomer–polymer particles which is a necessary condition for enhancement of modification by the portionwise addition of mercaptan.[15]

The previous section points out that the styrene–modifier emulsion droplets formed under the conditions outlined retain some of their identity during the remaining course of the polymerization. The reasons for this belief are: (1) the effectiveness of the styrene–mercaptan emulsion remains unchanged even after several weeks' storage at room temperature; (2) the beneficial modification is found despite the addition of the butadiene in completing the charging; and (3) the rate of polymerization in which preagitated styrene–mercaptan emulsion is used is significantly lower than that of the control. The first two reasons need no further elaboration because the stability of a hydrocarbon emulsion is well known, and data in this report show that mercaptan is depleting by a first-order reaction for an appreciable portion of the polymerization, Figure 6. However, the effect of preagitation on rate is worthy of further comment.

Omi and associates[16] have previously reported that the rate of polymerization of styrene preagitated with soap in a high-speed family mixer is significantly reduced. The reduced rate is attributed to less micellar soap remaining because of the soap adsorbed on the stabilized droplets. The reported reduced rate is similar to the reduction in rate found for our preagitated styrene–mercaptan emulsion even after the butadiene is charged. If the identity of the styrene–mercaptan droplets were not

TABLE V
Relative Rate of Polymerization for Fraction of Free Soap Remaining after Particles of
Different Diameters are Stabilized with Monolayers of Emulsifier

| Diameter of particle, Å | Fraction of free soap $(1 - 666/d)$ | Relative rate $(1 - 666/d)^{0.6}$ |
|---|---|---|
| 666[a] | 0 | 0 |
| 700 | 0.048 | 0.16 |
| 800 | 0.168 | 0.34 |
| 972 | 0.315 | 0.50 |
| 1000 | 0.334 | 0.52 |
| 2000 | 0.667 | 0.78 |
| 2145 | 0.690 | 0.80 |
| 5000 | 0.867 | 0.92 |
| 10000 | 0.933 | 0.96 |

[a] Calculated for 30 g styrene, 0.9 g/cm³, dispersed with a monomolecular layer from 5 g potassium oleate with a molecule area of 28 Å².

retained during charging and polymerization, the reduced rate and enhanced modification would not be found.

A relative rate of polymerization can be calculated by assuming that a monomolecular layer of soap covers the emulsion particles formed during preagitation and that the rate varies as the 0.6 power of the free soap. Further assumption was that the total area of a monomolecular layer, $S_t$, can be calculated by

$$S_t = N_A [S]a_s$$

where $N_A$ is Avogadro's number, [S] is moles of soap, and $a_s$ is area of a soap molecule. The relative rate of polymerization is

$$R_{rel} = (1 - S_t/S_d)^{0.6} = (1 - 666/d)^{0.6}$$

where $S_d$ is the area of soap covering particles from 30 g styrene with a diameter $d$, and 666 is the diameter for the maximum dispersion of the styrene particles if 5 g of potassium oleate with a molecular area of 28 Å² is all adsorbed as a monolayer on the particles. The relative rates obtained on the basis of the free soap that is not adsorbed on emulsion particles is shown in Table V. Under end-over-end laboratory bath agitation, monomer droplets of 1 micron in diameter have been estimated.[17] This size droplet would tie up only a small fraction of the soap. If vigorous agitation produced particles of 0.22 $\mu$ in diameter, about 30% of the soap would be adsorbed and the rate now would be only about 80% of the control rate. These are the orders of reduction of rates found in our study, Table II, and those reported in the literature for vigorously preagitated styrene–soap combinations.[16]

## Optimizing Modification by Preagitation

Previous studies relating modification efficiency to regulating index in SBR polymerizations showed that the highest efficiency is obtained with

modifiers having regulating indexes in the 3–4 range.[15] Modifiers with low indexes react too slowly and those with high indexes deplete too rapidly. Thus, Sulfole 160 mercaptan, a commercial $t$-$C_{16}$ mercaptan, requires 3.4 parts in the standard SBR 1500 recipe to give a Mooney viscosity of 50 ML-4. This same mercaptan when preagitated for 5 min with styrene and soap has a regulating index of 3.0, and only 0.39 parts per hundred of monomers is required for 50 ML-4. When allowance is made for purity, only 1.2 millimole of the hexadecyl modifier is needed to produce the standard Mooney viscosity. This compares to the 1 millimole of Sulfole 120 mercaptan, a commercial $t$-$C_{12}$ mercaptan.

In contrast to improvement for the $t$-$C_{16}$ mercaptan, preagitation of Sulfole 120 mercaptan increases the regulating index from 2.8 to 6.2. In requirements of modifier for a 50 Mooney viscosity, SBR 1500 polymer, this amounts to 0.20 and 0.23 phm, respectively, of Sulfole 120 mercaptan. Here, preagitation worsened modification for this mercaptan. Inadequate preemulsification of modifier is also undesirable as is shown by the experiments for the control polymerization where the modifier was preemulsified an inadequate time, Figure 9.

The most spectacular change in regulating index was obtained with $n$-dodecyl mercaptan, for which the index increased from 1.0 for the control to 16 for the preagitated system, Figure 6. The comparatively smaller change in regulating index for the tertiary isomer demonstrates why this modifier is less sensitive to factors influencing transport between phases than is the $n$-dodecyl mercaptan.

This report demonstrates that a continuous range of regulating indexes from 0.3 to 6 can be obtained by preagitation of the $t$-$C_{12}$ and of $t$-$C_{16}$ mercaptan in the SBR types of polymerization. The molecular weight distribution should vary as the regulating index does.

Preagitation of modifiers with the emulsifier introduces a new variable into emulsion polymerization systems.

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