

# Modification of Emulsion Polymerizations with Microemulsions of Mercaptans

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## Synopsis

Microemulsions of dodecyl and higher mercaptans are easily prepared with common surfactants and alkanol cosurfactants readily available in the emulsion polymerization industry. The reactivity of the microemulsified heavy mercaptan is greatly enhanced when properly prepared and charged. The regulating index of *tert*-hexadecyl mercaptan for a styrene-butadiene copolymerization (SBR) can be increased from 0.3 for the control to over 10 for the microemulsified modifier. Several ways of varying the reactivity of the modifier over a considerable range are presented. This article also presents solutions to some of the problems that arise in the preparation and use of the microemulsions. Applications of microemulsified mercaptans to modification of standard emulsion polymerizations are included. This method of enhancing the reactivity of modifiers is more practical than the preagitation technique previously reported.<sup>1</sup>

## INTRODUCTION

This is a continuation of the study of the efficient use of high-molecular-weight mercaptans as modifiers in emulsion polymerization systems as a means of reducing odor in these latexes and products. In a previous publication research on the effect of preagitating by mechanical means the modifiers or their solutions in monomers in the aqueous emulsifier solution was reported.<sup>1</sup> The macroemulsions made by the mechanical preagitation technique gave regulating indexes in polymerization systems that were the resultant of the reactivity of the modifier and intensity and duration of preagitation. For practical reasons, vigorous preagitation such as that obtained by ultrasonic irradiation or by means of a Waring Blendor were found necessary. This mechanical means of preparing the premacroemulsion of the modifier is unnecessary if the modifier is formed into a microemulsion by use of surfactant-cosurfactant combinations.

The preparation, theory, and application of microemulsions are reviewed in a recent chapter by Prince.<sup>2</sup> The reactions of highly dispersed high molecular weight compounds to hasten a reaction, such as hydrolysis of an ester, the reaction of compounds in the micellar state,<sup>3</sup> and interfacial syntheses<sup>4</sup> are examples of using colloidally dispersed reactants in organic syntheses. In the polymerization field, the work of Ugelstad and co-workers<sup>5</sup> shows how dispersions of monomers made with surfactant-cosurfactant combinations can be used to prepare uniform particle latex directly. The use of microemulsions of high-molecular-weight modifiers as a means of increasing the reactivity of these types of compounds in emulsion polymerization is, to the best of our knowledge, a new application of microemulsions.

This report presents data on the preparation of microemulsions of C<sub>12</sub> and higher normal and tertiary mercaptans. Some work with special macroemulsions is also presented. Solutions to most of the problems encountered with the use of microemulsions in emulsion polymerization systems are given.

## EXPERIMENTAL

### Materials

Commercial *t*-dodecyl (*t*-C<sub>12</sub>); a 60/20/20 mix of *t*-dodecyl/*t*-tetradecyl/*t*-hexadecyl (*t*-C<sub>13,2</sub>); *t*-hexadecyl (*t*-C<sub>16</sub>) mercaptans ("Sulfole" mercaptans, Phillips); and *n*-dodecyl mercaptans have been described previously<sup>6</sup>; and *n*-tetra, *n*-hexa, and *n*-octadecyl mercaptans (Humphry Chemical) were all used as received.

Commercial rosin soap (Dresinate 554 and Dresinate 979, Hercules), fatty acid (P59, Proctor and Gamble), petroleum sulfonate (TRS 10-410, Witco Chemical), and sodium lauryl sulfonate (commercial supplier) were used as received. Iso-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-octanol, *n*-dodecanol, and *n*-tetradecanol were used as obtained from commercial suppliers.

The butadiene (Phillips Petroleum Co.) was flashed, passed over activated alumina, and stored at -20°C until used. Styrene (Dow), chloroprene (Pfaltz and Baurer), acrylonitrile (Eastman), and ethyl acrylate (Rohm and Haas) were distilled at reduced pressure and stored at -20°C until used. *p*-Menthane hydroperoxide (Hercules), sodium formaldehyde sulfoxylate (Eastman), tetrahydrate of tetrasodium ethylenediaminetetraacetic acid (Stauffer), inorganic salts (Mallinckrodt), Thiostop N shortstop (Uniroyal), and Flexzone 7L antioxidants (Uniroyal) were those commonly used in the SBR industry.

### Polymerization Recipes

The standard SBR 1500 and 1503 formulations<sup>7,8</sup> were used for most of the exploratory work, and the applications were made with standard and high solids SBR and NBR, CR, ABR, and acrylate-styrene emulsion polymerizations. Polymerizations were conducted by the bottle technique.<sup>9</sup> In the majority of the exploratory experiments, the amount of microemulsion used was that containing 0.5 to 0.92 parts per hundred monomers (phm) (1.56-2.85 mmole) of Sulfole 160 mercaptan (Phillips), or with other modifiers, the amounts of microemulsions containing these equivalent amounts were charged. When no amount is given, the amount of microemulsion containing 0.5 phm of modifier was used.

### Microemulsions

The definition of a microemulsion (ME) used here is that given by others<sup>2</sup>: a stable dispersion of one liquid in another in the form of spherical droplets, the diameters of which are less than one quarter the wavelength of white light (0.25  $\lambda$ ) or approximately 0.14  $\mu$  (1400 Å). This means the dispersions were at least translucent and highly stable. Although most of the dispersions of the mercaptans fitted these requirements, some dispersions used were of large particle sizes, opaque, separated into two or more phases, and classed as macroemulsions.

The majority of the microemulsions were prepared in accordance with a standard formulation, Table I, and the following procedure. The standard procedure was to add the modifier to a concentrated solution of the surfactant, such as the petroleum sulfonate or Dresinate 554 as received, dilute with 40-55

TABLE I  
Standard Formulation for Microemulsions of Modifiers

	Parts
Modifier	40
Water	40-55
Surfactant	5-20
KCl	0.4-0.5
Cosurfactant	variable
Temperature	ambient

parts of the 1.0% KCl solution, agitate by hand or magnetic bar until homogeneous, and then add the cosurfactant with stirring until the dispersion becomes translucent or transparent. Agitation was by a magnetic bar at 350-450 rpm or by a vertical 30.5-cm stroke at about 120/min. Most preparations were conducted in closed vessels or capped bottles under a nitrogen atmosphere.

Variations of the preceding procedure were replacing part of the modifier with an inert solvent or styrene, using less than 5 parts of the surfactant, adding additional modifier to an already formed microemulsion, and variations of the polymerization charging procedure which could be classed as microemulsion preparations.

### Charging Microemulsions

Of the charging procedures tried, three were used most often: (1) a specified amount of microemulsion weighed in a syringe was added dropwise into the static polymerization emulsifier solution; (2) the weighed microemulsion was added dropwise into a swirling polymerization emulsifier solution; (3) and the weighed microemulsion was injected forcibly from the syringe into the swirling polymerization emulsifier solution. The polymerization emulsifier solution also contained the auxiliary dispersant, electrolyte, and base for adjustment to the proper pH. Styrene, butadiene, and *p*-menthane hydroperoxide were charged in that order. The bottles were preemulsified in the bath for 1/2 hr before initiating with the sulfoxylate activator. However, charging order and method of adding the microemulsion were found to be important, and these charging variations are included in a subsequent section.

### Particle Size Determination

Light scattering photometry was used to measure the particle size of the microemulsion after being dispersed by dropwise addition of 0.3 ml of microemulsion to 100 ml of static polymerization emulsifier solution. Dissymmetry ratio,  $Z = i_{45^\circ}/i_{135^\circ}$ , was converted to particle diameter  $D$  (Å), using a plot of  $Z$  vs.  $D$  calculated for monodispersed spheres.<sup>10</sup> Decreasing the amount of microemulsion by one half made no difference in the measured particle size of the dispersed microemulsion.

## Regulating Index

Mercaptan depletion was followed by sampling the polymerization periodically and determining the mercaptan by the Kolthoff-Harris amperometric titration procedure.<sup>11</sup> The regulating index  $r$  is defined by  $d(\ln S)/dX = -r$ . The value of  $r$  is obtained as the slope of an  $\ln S$ - $X$  plot;  $S$  is the amount of mercaptan in percentage remaining and  $X$  is the fractional conversion of monomer. The significance of the value of  $r$  with respect to controlling the molecular weight of SBR polymers is discussed in a recent publication.<sup>12</sup>

## RESULTS

### Microemulsion Preparation Variables

Figure 1 shows the depletion curves for an SBR 1500 system for the  $t$ -C<sub>16</sub> mercaptan control and for microemulsions made with 5, 10, and 20 parts of Witco TRS 10-410 petroleum sulfonate and with 0.12, 0.24, and 0.48 parts of hexanol as cosurfactant. Although the microemulsion made with 5 parts of the petroleum sulfonate was not translucent (it resembled skimmed milk), thin films of the dispersion exhibited the bluish and reddish Tyndall coloration with reflected and transmitted white light. This is characteristic of a dispersion consisting of a mixture of particles with a majority in the Tyndall range and a minority larger than 1500 Å in diameter.

Another procedure of preparing a series of microemulsions with variable amounts of surfactant is to use variable portions of the microemulsion with the highest surfactant concentration and then add the amount of modifier and salt solution to give the proper proportion of the various ingredients. Table II shows the data for preparing a series of microemulsions with  $t$ -C<sub>16</sub> mercaptan by the standard procedure and preparing the similar series by using one-half or one-fourth of the 20-part surfactant microemulsion and then adding the mercaptan and potassium chloride solution to give the specified porportion of ingredients.

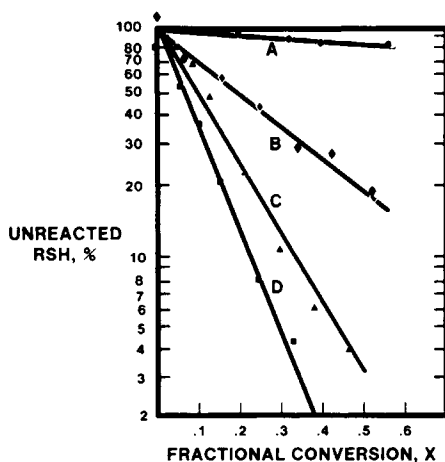


Fig. 1. Mercaptan depletion for petroleum sulfonate- $t$ -C<sub>16</sub> mercaptan microemulsion in an SBR 1500 recipe. Parts of surfactant: B, 5; C, 10; D, 20; A, neat  $t$ -C<sub>16</sub> mercaptan control. Experimental data Table II.

TABLE II  
Modifications with and Preparation of Microemulsions of *t*-C<sub>16</sub>SH by Direct Procedure and by Using Portions of the Most Concentrated Microemulsion

Make-up procedure	Petroleum sulfonate, g	Hexanol, g	Pzn. rate, %/hr	Regulating index, <i>r</i> <sup>a</sup>	Inherent visc., l./g <sup>b</sup>
Direct	20	0.48	8.7	10.3	0.296
Direct	10	0.24	8.3	7.7	0.215
Direct	5	0.12	8.8	4.0	0.159
Portion <sup>c</sup>	10	0.24	8.3	7.7	0.218
Portion <sup>d</sup>	5	0.12	9.1	4.0	0.166

<sup>a</sup> Charging procedure for ME was A.

<sup>b</sup> *t*-C<sub>16</sub>SH amount averaged 0.72 phm.

<sup>c</sup> One-half of the ME made with 20 g surfactant.

<sup>d</sup> One-fourth of the ME made with 20 g surfactant.

The data in Table II show that the regulating index varies with the surfactant-cosurfactant levels, and some of the *r* values are considerably higher than those obtained by the preagitation technique.<sup>1</sup>

With 10 parts of Dresinate 554 surfactant, the effect of two recipe variables, different alkanol cosurfactants, and percentage neutralization of the rosin acid; and with 10 parts of petroleum sulfonate surfactant, the effect of different salts for microemulsifying *t*-C<sub>16</sub> mercaptan were tested in the SBR system (Table III).

Combinations of petroleum sulfonate surfactant and propanol, butanol, and

TABLE III  
Effect of Variable Cosurfactant and Neutralization with Dresinate 554 Surfactant and Different Salts with Petroleum Sulfonate on Microemulsifying *t*-C<sub>16</sub> Mercaptan

Variable	Amount	ME charge procedure	Pzn. rate, %/hr	Regulating index <i>r</i>	Inherent visc., l./g <sup>c</sup>
<i>Dresinate 554 Surfactant</i> <sup>a</sup>					
Hexanol	1.63 g	A	8.5	6.2	0.224
Octanol	1.45 g	A	8.5	5.6	0.204
Decanol	1.66 g	A	8.5	6.0	0.212
Dodecanol	1.83 g	A	8.5	5.6	0.200
Tetradecanol	2.47 g	A	8.5	6.7	0.230
<i>Dresinate 554 Surfactant</i> <sup>b</sup>					
Neutralized	85%	C	8.5	9.4	0.317
Neutralized	95%	C	8.5	12.4	0.377
Neutralized	100%	C	8.5	13.6	0.407
Neutralized	105%	C	8.5	13.1	0.380
Neutralized	115%	C	8.5	12.4	0.374
<i>Petroleum Sulfonate Surfactant</i> <sup>b</sup>					
KCl	0.4 g	C	8.0	5.9	0.214
K <sub>2</sub> CO <sub>3</sub>	0.4 g	C	8.0	6.7	0.247
K <sub>3</sub> PO <sub>4</sub>	0.4 g	C	8.0	6.7	0.243
KH <sub>2</sub> PO <sub>4</sub>	0.4 g	C	8.0	6.9	0.256
K <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·5H <sub>2</sub> O	0.4 g	C	8.0	6.1	0.216
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0.4 g	C	8.0	6.2	0.219

<sup>a</sup> Dresinate 554 used as received.

<sup>b</sup> Hexanol cosurfactant.

<sup>c</sup> *t*-C<sub>16</sub>SH = 0.5 phm.

pentanol cosurfactant were also used to prepare microemulsions of the *t*-hexadecyl mercaptan. Hexanol, however, seemed to be the preferred cosurfactant for a number of different microemulsions that were examined during the course of this study. Some of these will be reported in this section of the report.

The data in Table III show that the different alkanol cosurfactants and different anions have a relatively small effect on the reactivity of the microemulsified modifier, but the method of charging and the neutralization of the surfactant have significant effects on modification.

The data in Table II and Figure 1 show that the regulating index varied with the petroleum sulfonate-cosurfactant level. A method was sought for controlling the regulating index between the value of about 4 for the microemulsion and 0.3 for the neat *t*-C<sub>16</sub> mercaptan as the modifier in the SBR 1500 system. Using lower amounts of surfactants or different surfactants at these low levels resulted in unstable emulsions even though the latter gave lower regulating indexes. Diluting the mercaptan with inert diluents gave the desired result. The data in Figure 2 show the variation in the regulating index of Sulfole 160 mercaptan as different ratios of the modifier and dodecane were microemulsified with five parts of petroleum sulfonate.

Microemulsions were prepared with surface active agents commonly used in the SBR industry. Different rosin acid soaps, fatty acid soaps, potassium soap flakes, and sodium lauryl sulfate were used to microemulsify the *t*-C<sub>16</sub> mercaptan. All gave stable microemulsions and enhanced the modification of the heavy mercaptans in the SBR 1500 systems. Examples of different mercaptans microemulsified with potassium fatty acid surfactant are given in Table IV.

Three differences are noted between the preparation and reactivity of the microemulsion prepared with potassium fatty acid and those made with the two previous emulsifiers in Tables II and III. Much more electrolyte and cosurfactant were needed for a stable dispersion, the reactivity of the *t*-C<sub>16</sub> mercaptan was high, and a high rate of depletion of the modifiers was found during the first 10% of conversion (this is named as abnormal depletion). These results emphasize that a considerable variation exists between the microemulsions prepared with different surfactants. Before considering these differences further, another variable should be examined first.

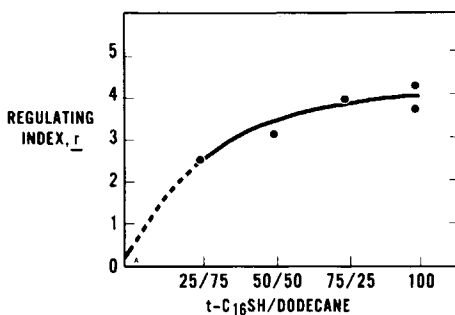


Fig. 2. Effect of variable ratios of *t*-C<sub>16</sub> mercaptan and dodecane on the regulating index of the microemulsified blends with 5 parts of petroleum sulfonate. (a) Neat mercaptan control.

TABLE IV  
Different Mercaptans Microemulsified With 20 g Potassium Fatty Acid Surfactant and Tested in the SBR 1503 Recipe

Mercaptan	Hexanol, g	Addnl. KCl, g <sup>a</sup>	Pzn. rate, %/hr	Regulating index <i>r</i> <sup>b</sup>	Mooney ML-4 <sup>c</sup>
<i>t</i> -C <sub>12</sub>	10.5	2.9	8.7	6.7	16
<i>n</i> -C <sub>12</sub>	9.6	2.9	9.5	21.5	110
<i>t</i> -C <sub>13.2</sub>	10.54	2.9	8.6	6.4	19
<i>t</i> -C <sub>16</sub>	9.66	2.9	8.7	15.1	93
<i>n</i> -C <sub>18</sub> <sup>d</sup>	9.70	2.9	10.3	1.9	134

<sup>a</sup> Additional KCl in 10 ml of saturated solution plus 10 ml water were needed to make a stable microemulsion.

<sup>b</sup> All modifiers showed abnormally high depletion during the first 10% of conversion.

<sup>c</sup> Modifier level was 0.78 phm.

<sup>d</sup> Macroemulsion.

### Order and Method of Charging

Early in this study, a marked difference in mercaptan depletion was noted when the microemulsion was added to the soap solution layer rather than the styrene layer as was done with the neat mercaptan. This is shown by a series of experiments in which the order and method of charging was varied for a petroleum sulfonate microemulsified *t*-C<sub>16</sub> mercaptan in an SBR 1500 recipe, Table V.

Adding the microemulsion dropwise into the styrene layer resulted in a destruction of the effectiveness of the microemulsion, which could be partially overcome by forcibly injecting the microemulsion through the styrene layer into the soap solution. Injecting the microemulsion under the surface of the stirred soap solution gave the highest regulating index, but adding the microemulsion to preemulsified styrene or monomer mixture resulted in the most efficient modification (Table V).

The same series of experiments conducted with the Dresinate 554 microemulsion exhibited essentially the same trends in mercaptan depletion with charge order and method as did the petroleum sulfonate microemulsion.

TABLE V  
Effect of Order or Method of Adding a Petroleum Sulfonate-*t*-C<sub>16</sub> Mercaptan Microemulsion on Depletion in the SBR 1500 Recipe

Charging order or method of adding ME <sup>a</sup>	Pzn. rate, %/hr	Regulating Index <i>r</i>	Inherent visc., l/g
Dropwise to soap solution	8.5	5.1	0.201
Inject into soap solution	8.5	6.0	0.136
Down side of bottle into soap soln.	8.5	5.1	0.168
Injected under stirred soap soln.	8.5	6.7	0.162
Dropwise into styrene layer	9.2	0.4	0.343
Injected thru styrene layer	8.5	— <sup>b</sup>	0.186
Styrene, ME, soap soln.	9.2	0.2	0.413
Dropwise to thick styrene layer	9.2	0.3	0.391
Dropwise into emulsified styrene	8.5	4.8	0.123
Add ME at time of activation	8.5	4.1	0.113

<sup>a</sup> *t*-C<sub>16</sub>SH, 0.92 phm.

<sup>b</sup> Nonlinear depletion curve.

However, the Dresinate series did not show as drastic a decrease in modification on addition of the microemulsion to styrene as did the petroleum sulfonate series.

In another variation of charging, 30 parts of styrene of the SBR 1500 recipe were microemulsified with the 4.6 parts of Dresinate 554 soap in 40 parts of water and 1.62 parts of hexanol cosurfactant, and then 0.5 phm of five mercaptans was added to the styrene microemulsion before the charging was completed. The ingredients were preemulsified for 30 min at bath temperature before activating in the standard manner (Table VI).

In another variation of charging, the recipe amount of mercaptan was added to a concentrated soap solution (40 parts water and 4.6 phm of Dresinate 554) and variable amounts of hexanol were added before the remainder of the makeup water was added for the soap solution. For this series the regulating index of the *t*-C<sub>16</sub> mercaptan varied from 0.85 to 5.22 for the runs with zero to 1.4 phm hexanol, respectively. The appearance of these emulsions varied from opaque to clear as the amount of alcohol was increased. However, all the runs exhibited some loss of mercaptan before initiation and variable degrees of abnormal depletion of mercaptan during the first 10% of polymerization.

When Dresinate 554-*t*-C<sub>16</sub> mercaptan microemulsion is charged to the recipe soap solution, a slight cloudiness or haze is formed. If 0.84 ml hexanol is added to the recipe soap solution before the microemulsion is added, the soap solution remains clear. When the remaining recipe ingredients are charged, some mercaptan is lost before initiation and abnormal depletion during the first 10% of conversion occurs followed by a more normal depletion rate, curve B. However, if the microemulsion is charged just before initiation, a normal depletion curve is obtained, curve A. The depletion curves for these two charging variations are given in Figure 3.

The data in this section on charging microemulsions of modifiers show that considerable variation in reactivity can be obtained by varying charge order or the method of charging. In the following section, incremental addition is another variation of charging that deserves attention.

### Incremental Addition

The high regulating index of microemulsified *t*-C<sub>16</sub> mercaptan indicates this modifier should show enhanced modification if charged incrementally. However, when the *t*-C<sub>16</sub> mercaptan-petroleum sulfonate microemulsion was added in

TABLE VI  
Effect on Modification of Microemulsifying the Styrene before Adding Mercaptans in the SBR 1500 System

Mercaptan	Pzn. rate, %/hr	Regulating index <i>r</i>	Inherent viscosity, l./g
<i>t</i> -C <sub>13.2</sub>	7.6	5.2 <sup>a</sup>	0.095
<i>t</i> -C <sub>16</sub>	7.5	4.9 <sup>a</sup>	0.106
<i>n</i> -C <sub>12</sub>	7.7	2.7 <sup>b</sup>	0.234
<i>n</i> -C <sub>14</sub>	7.6	4.9 <sup>a</sup>	0.180
<i>n</i> -C <sub>16</sub>	8.3	3.1 <sup>a</sup>	0.416

<sup>a</sup> Some abnormal depletion during the first 10% conversion.

<sup>b</sup> Large abnormal depletion during the first 10% conversion.



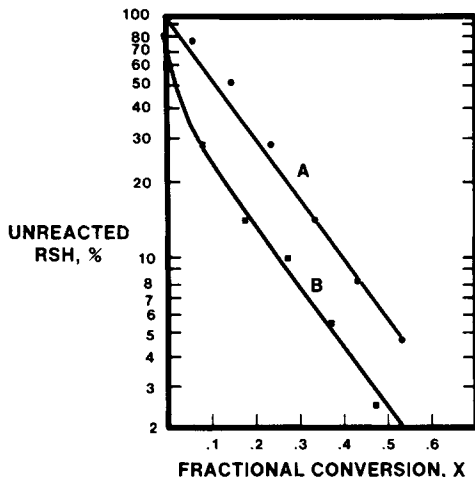


Fig. 3. Effect of two charge orders on modification depletion: A, microemulsion charged just prior to activation; B, normal charge order, control.

two increments to the SBR 1500 system, modification was poorer than the control with all modifiers added originally. A modifier depletion study of this system revealed why the incremental addition run did not work with the microemulsion (Fig. 4). Evidently, the second increment of the microemulsion was destroyed since the depletion rate after the second increment is that expected for a blend of two modifiers with the different  $r$  values.<sup>13</sup> Apparently, the environment into which the second increment was injected was too different for the microemulsion to retain its identity. When the second increment was preconditioned by first being added to 5 ml of the recipe soap solution, the increment behaved in a desired manner (Fig. 4).

Fortunately, the  $t$ -C<sub>16</sub> mercaptan microemulsified with Dresinate soap and added incrementally to the SBR 1500 system depleted in the expected manner and resembled curve B in Figure 4.

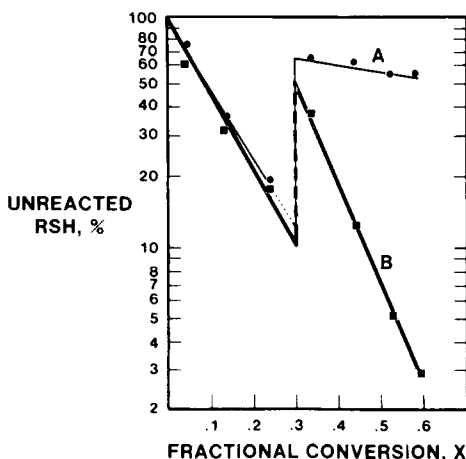


Fig. 4. Incremental addition of  $t$ -C<sub>16</sub> mercaptan-petroleum sulfonate microemulsion: A, increment of microemulsion added as originally prepared; B, increment preconditioned by injecting into Dresinate soap solution before adding to polymerizing latex.

The enhancement of modification obtained with *t*-C<sub>16</sub> mercaptan–Dresinate microemulsion added incrementally is shown by the curves in Figure 5. Two variations of adding two levels of the microemulsions were tried. In both cases the first increment was added at zero and the second at a later conversion.

### Particle Sizes of Diluted Microemulsions

The visual appearance of the microemulsions of the modifiers varied from transparent to various degrees of translucency to opacity. Some of the latter dispersions displayed Tyndall scattering when viewed with transmitted or incident light. These qualitative characteristics indicate that the particle sizes of these dispersions have diameters close to and below the wavelength of white light. The addition of these dispersions to the full amount of the polymerization soap solution usually resulted in a slight increase in haziness of the resultant dispersion. This suggested the original dispersion might retain its identity in the soap solution and could be measured by a light scattering technique. The data in Table VII show the particle size diameter obtained by light scattering of the diluted dispersion of some of the microemulsions that have been reported in previous sections of this report. With a density of 0.86 g/ml for the mercaptans and diluents, the surface area of particles were calculated and the values were plotted against their regulating indexes (Fig. 6).

Despite the variables attending the preparation of the different microemulsions, the dilution of the microemulsion, the light scattering measurements, and the polymerization complexities, the plot of data seems to show a relationship between the measured particle size and regulating index. These data support the belief that the microemulsions maintain their identity during the course of the polymerization. However, there are no measurements proving that the microemulsion sizes in the polymerizing system are the same as they are in the recipe soap solution.

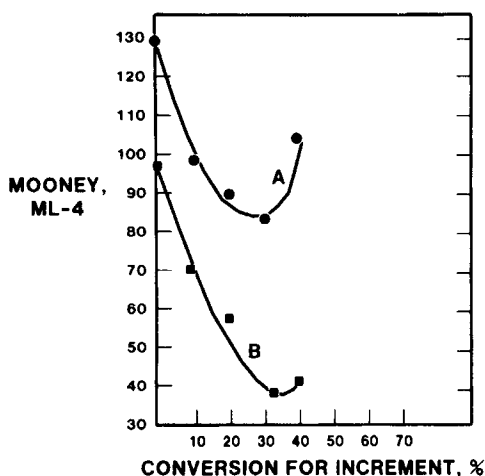


Fig. 5. Mooney vs. conversion for increment of the *t*-C<sub>16</sub> mercaptan–dresinate microemulsion in the SBR 1500 recipe. Variations: A, microemulsion contained 0.38 phm *t*-C<sub>16</sub>SH divided 1/2, 1/2; B, microemulsion contained 0.5 phm *t*-C<sub>16</sub>SH divided 2/3, 1/3.

TABLE VII  
Particle Size Measurements by Light Scattering of Microemulsions Diluted in a Recipe Dresinate Soap Solution

Mercaptan		Surfactant		Hexanol, g	Regulating index $r$	$D, \text{\AA}$	Area, $\text{m}^2/\text{g}$
Type	Amt.	Type	Amt.				
<i>t</i> -C <sub>16</sub>	40	PS <sup>a</sup>	5	0.16	4.2	1120	62.3
<i>t</i> -C <sub>16</sub>	40	PS	10	0.16	8.2	790	88.4
<i>t</i> -C <sub>16</sub>	40	PS	20	0.81	8.7	820	85
<i>t</i> -C <sub>16</sub>	40	PS	20	0.24	10.3	760	91.7
<i>t</i> -C <sub>16</sub>	40	PS	20	0	7.6	1020	68.4
<i>t</i> -C <sub>16</sub>	40	PS	20	1.62	8.4	1030	67.8
<i>t</i> -C <sub>16</sub>	40	PS	5	0.18	3.7	1000	69.8
<i>t</i> -C <sub>16</sub> /C <sub>14</sub> <sup>b</sup>	30	PS	5	0.12	3.9	1340	52.1
<i>t</i> -C <sub>16</sub> /C <sub>14</sub> <sup>b</sup>	20	PS	5	0.12	3.1	1330	52.4
<i>t</i> -C <sub>16</sub> /C <sub>14</sub> <sup>b</sup>	10	PS	5	0.12	2.5	1480	47.1
<i>n</i> -C <sub>18</sub> /C <sub>16</sub> <sup>c</sup>	15	PS <sup>d</sup>	8	2 <sup>e,f</sup>	4.4	1050	66.5
<i>n</i> -C <sub>18</sub> /C <sub>16</sub> <sup>c</sup>	15	PS <sup>d</sup>	8	2 <sup>e,g</sup>	5.3	910	76.7

<sup>a</sup> Petroleum sulfonate surfactant.

<sup>b</sup> Mercaptan + *n*-tetradecane = 40.

<sup>c</sup> 15 parts *n*-C<sub>18</sub>SH/15 parts *n*-hexadecane.

<sup>d</sup> Experimental petroleum sulfonate surfactant.

<sup>e</sup> Pentanol, 2 g, in place of hexanol.

<sup>f</sup> NaCl, 0.2 g, for KCl.

<sup>g</sup> No added electrolyte.

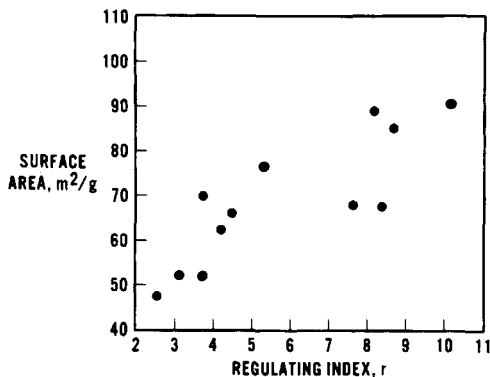


Fig. 6. Surface area vs. regulating index of microemulsions of mercaptans diluted in a recipe soap solution and measured by light scattering. Data in Table VII.

### Modification of Standard SBR Recipes

Figure 7 shows the depletion curves for neat Sulfole 120 and microemulsified Sulfole 160 mercaptans with approximately the same reactivity in the SBR 1500 recipe. The marked similarity of the two curves with a discontinuity appearing at about 50% conversion suggests that the modifiers are depleting by similar mechanisms.

In Figure 8 the modifier requirement data for two controls, neat Sulfole 120 and 160 mercaptans, and for Sulfole 160-Witco TRS 10-410 microemulsion in the SBR 1500 recipe are plotted. The regulating indexes for the *t*-C<sub>12</sub> and the microemulsified *t*-C<sub>16</sub> mercaptan were approximately the same.

The mercaptan requirements interpolations were used as guides for preparing samples for evaluation of SBR 1500 type of polymers. The characterization data are given in Table VIII, and the evaluation data for tread stocks for the two polymers are in Table IX.

High-conversion SBR 1712-type copolymers were prepared with the *t*-C<sub>12</sub> mercaptan control and with the microemulsified *t*-C<sub>16</sub> mercaptan. The re-

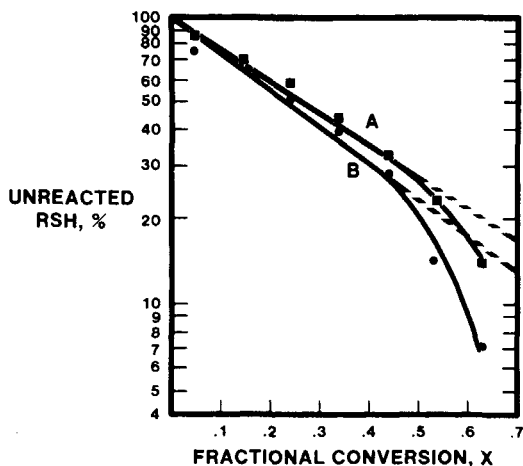


Fig. 7. Depletion for neat sulfole 120 and microemulsified sulfole 160 mercaptans in the SBR 1500 systems: A, microemulsified *t*-C<sub>16</sub> mercaptan;  $r = 2.6$ ; B, neat *t*-C<sub>12</sub> mercaptan,  $r = 2.85$ .

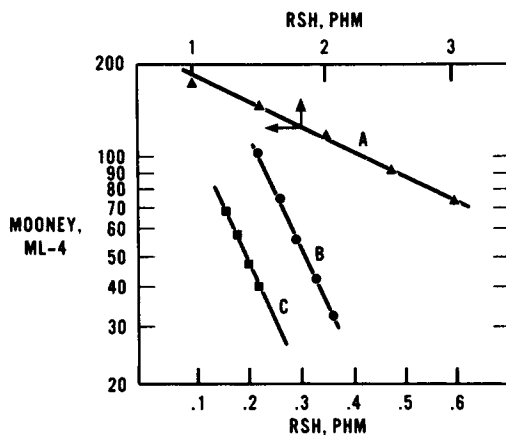


Fig. 8. Mercaptan requirement for *t*-C and *t*-C<sub>16</sub> mercaptan controls and for *t*-C<sub>16</sub> mercaptan-petroleum sulfonate microemulsion: A, neat *t*-C<sub>16</sub> mercaptan control; B, *t*-C<sub>16</sub> mercaptan microemulsion; C, neat *t*-C<sub>12</sub> mercaptan control.

quirements for a 50 Mooney viscosity polymer were 0.7 and 0.9 mmole per hundred monomer for the two modifiers, respectively. The characterization and the evaluation data indicated the experimental polymer had a broader molecular weight distribution than the control. No effort was made to optimize the microemulsion for the preparation of the high-conversion polymer. Possibly different reactivities would be required for the experimental modifier to give a more narrow molecular weight distribution at the higher conversions.

### Modification of High-Solids Latexes

Neat *n*- and *t*-C<sub>12</sub> and neat *t*-C<sub>16</sub> mercaptans were compared to these mercaptans microemulsified with 10 parts of neutralized Dresinate 554 surfactant in a low water (70 phm), high-solids recipe.<sup>18</sup> Neat *t*-C<sub>12</sub> and *t*-C<sub>16</sub> mercaptans were compared with only the *t*-C<sub>16</sub> mercaptan microemulsified with 5 and 10 parts of neutralized Dresinate 554 surfactant in a high-water (170 phm), low-solids recipe. The latter latex recipe is similar to the first except that 2.85 parts of potassium oleate was charged initially as the sole emulsifier.<sup>18</sup> The microemulsified modifiers were added just prior to activation after emulsifying the other ingredients at 5°C for 30 min. The experimental data for the two series of polymerizations are given in Table X.

TABLE VIII  
Characterization Data for SBR 1500 Polymers Prepared with *t*-C<sub>12</sub> Mercaptan Control and with *t*-C<sub>16</sub> Mercaptan-Petroleum Sulfonate Microemulsion Modifiers

Mercaptan Type	PHM	Inherent visc., l./g	GPC		Mooney ML-4	
			$\bar{G}^a$	HI		
<i>t</i> -C <sub>12</sub>	0.20 <sup>c</sup>	0.198	0.76	3.2	391/124	54
<i>t</i> -C <sub>16</sub> ME	0.38 <sup>d</sup>	0.182	0.83	3.1	304/98	44

<sup>a</sup>  $\bar{G}$  is average branching.<sup>17</sup>

<sup>b</sup> All  $\bar{M}_s \times 10^{-3}$ .

<sup>c</sup> 1 mmole.

<sup>d</sup> 1.24 mmole.

TABLE IX  
Vulcanize Data for SBR 1500 Rubber Prepared with *t*-C<sub>12</sub> Mercaptan Control and with  
Microemulsified *t*-C<sub>16</sub> Mercaptan Modifiers

Modifier	Control <i>t</i> -C <sub>12</sub> SH	Microemulsion <i>t</i> -C <sub>16</sub> SH	SBR 1500
Original, ML-4	54	44	54
Compound, ML-4	60	51	59
Tread Cure 150°C, 30 min <sup>a</sup>			
Compression set, %	27.2	29	27.5
300% Modulus, MPa	8.4	7.1	8.6
Tensile, MPa	24.4	24.0	24.6
Elongation, %	660	705	640
Heat buildup, $\Delta T$ , °C	46.2	51.2	49.2
Resilience, %	56.2	53.2	54.2
Shore Hardness A	60	60	60

<sup>a</sup> Other ingredients/100 rubber: N330 black, 50; Philrich 5 oil, 10; ZnO, 3; stearic acid, 1; Flexamine, 1; sulfur, 1.75; Santocure, 1.2.

The *n*-dodecyl mercaptan was inefficient when charged in either form to the high-solids recipe, as is the case when this modifier is used in other low-temperature SBR recipes.<sup>1</sup> The *t*-dodecyl mercaptan was the most efficient modifier charged neat and is usually the modifier of choice for high-solids polymerization systems.<sup>18</sup> Microemulsifying *t*-C<sub>12</sub> mercaptan raised the reactivity to the point the efficiency is lower than that of the control. Microemulsifying the *t*-hexadecyl mercaptan with 5 parts of surfactant raised the regulating index to an efficient range, from 0.2 to 2.1, while 10 parts of Dresinate surfactant increased the activity to an inefficient limit,  $r > 6$ . These results emphasize the necessity of correctly formulating the microemulsion to the latex system in which the modifier is being used.

### Modification of Chloroprene

Chloroprene emulsified with Dresinate soap and initiated with presulfate was polymerized at 15°C in presence of neat and microemulsified mercaptans. The *n*- and *t*-dodecyl mercaptans were microemulsified with Dresinate 554 surfactant, and *t*-hexadecyl and *n*-octadecyl mercaptans were dispersed with petroleum sulfonate surfactant. Some of the polymerization and characterization data of the polychloroprene are given in Table XI, and the pair of GPC curves for polymers modified with the *t*- and *n*-dodecyl mercaptan are plotted in Figure 9.

The transfer constants for neat *n*- and *t*-dodecyl mercaptans are fairly close to some values reported in the literature,<sup>19</sup> and the inherent viscosities and GPC curves follow in an expected manner. The transfer constants found for *t*-hexadecyl and *n*-octadecyl mercaptans were higher than expected in comparison to the lower homologs, and the modification was not as efficient as expected on basis of the modification parameters. This unpredicted behavior might find its explanation in the exceptional polymerization and modification kinetics reported for chloroprene in emulsion systems.<sup>20</sup>

TABLE X  
Neat and Microemulsified Mercaptans in High-Solids Recipes

H <sub>2</sub> O, phm	Mercaptan		Conversion, % at (hr)	Index <i>r</i>	Inh. visc., l./g	Gel, %
	Type	Added				
70	<i>n</i> -C <sub>12</sub>	0.5 neat	62(24)	0.6	0.37	8
70	<i>t</i> -C <sub>12</sub>	0.5 neat	62(24)	2.0	0.13	0
70	<i>t</i> -C <sub>16</sub>	0.5 neat	62(24)	0.7	0.31	89
70	<i>n</i> -C <sub>12</sub>	0.5 ME	61(24)	2.7	0.30	10
70	<i>t</i> -C <sub>12</sub>	0.5 ME	61(24)	6.0	0.15	0
70	<i>t</i> -C <sub>16</sub>	0.5 ME	61(24)	3.6	0.20	0
170	<i>t</i> -C <sub>12</sub>	0.08 neat	69(11.5)	—	0.39	0
170	<i>t</i> -C <sub>12</sub>	0.5 neat	65(11.5)	1.6	0.094	0
170	<i>t</i> -C <sub>16</sub>	0.5 neat	68(11.5)	0.2	0.38	0
170	<i>t</i> -C <sub>16</sub>	0.5 ME <sup>a</sup>	70(11.5)	2.1	0.21	0
170	<i>t</i> -C <sub>16</sub>	0.5 ME <sup>b</sup>	68(11.5)	9.2	0.44	0

<sup>a</sup> With 5 parts neutralized Dresinate 554 surfactant.

<sup>b</sup> With 10 parts neutralized Dresinate 554 surfactant.

TABLE XI  
Modifying Chloroprene Emulsion Polymerization with Neat and Microemulsified Mercaptans

Mercaptan <sup>a</sup>	Added	Pzn. rate, %/hr	$C_{tr}$ <sup>b</sup>	Inherent visc., l./g <sup>c</sup>	Gel, %	$HI$ <sup>d</sup>
<i>n</i> -C <sub>12</sub>	neat	7.0	0.76	0.101	0	2.67
<i>n</i> -C <sub>12</sub>	ME	8.0	1.06	0.064	0	2.20
<i>t</i> -C <sub>12</sub>	neat	9.8	0.30	0.218	0	5.54
<i>t</i> -C <sub>12</sub>	ME	8.6	0.33	0.150	0	3.00
<i>t</i> -C <sub>16</sub>	neat	9.9	0.51	0.269 <sup>e</sup>	96	—
<i>t</i> -C <sub>16</sub>	ME	9.9	0.87	0.273	0	—
<i>n</i> -C <sub>18</sub>	ME	9.4	1.15	0.145 <sup>e</sup>	63	—

<sup>a</sup> Approximately 0.5 phm.

<sup>b</sup> Transfer constant.

<sup>c</sup> Determined in toluene solvent.

<sup>d</sup> Relative heterogeneity index based on standard polystyrene calibration curve and determined in THF.<sup>17</sup>

<sup>e</sup> Soluble portion only.

### Modification of Butadiene–Acrylonitrile, Butadiene–Ethyl Acrylate, and Styrene–Ethyl Acrylate Copolymers

The first two monomer pairs, butadiene–acrylonitrile and butadiene–ethyl acrylate, at a 70/30 ratio were modified with neat and microemulsified *t*-C<sub>12</sub> and *t*-C<sub>16</sub> mercaptans. The microdispersions were made at the 10-part surfactant level with either petroleum sulfonate or Dresinate 554 surfactants. The styrene–ethyl acrylate pairs were charged at 50/50 and 75/25 monomer ratios and were modified with only the neat and microemulsified *t*-C<sub>16</sub> mercaptans. In these three sets of experiments, the modifiers were added just prior to initiation and were not present during the 30-min preemulsification step. The experimental data for these four pairs of monomers are given in Table XII.

The results for the monomer pairs in Table XII modified with neat and microemulsified *t*-C<sub>12</sub> mercaptans show that the neat modifier was the more efficient and no advantage was gained by microemulsifying this modifier for these

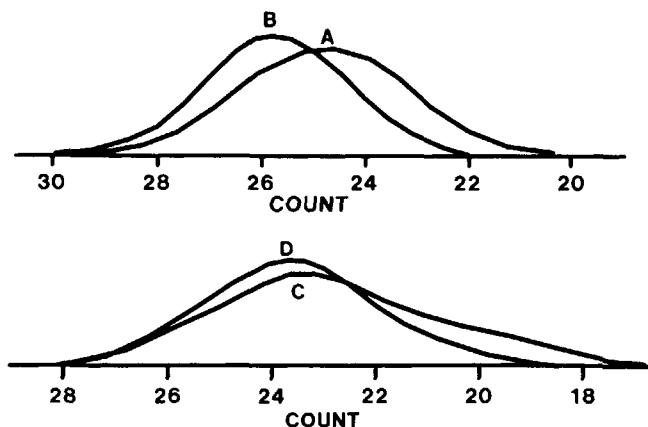


Fig. 9. GPC curves for polychloroprene modified with A, neat *n*-dodecyl mercaptan and B, with the modifier microemulsified: C, neat *t*-dodecyl mercaptan, and D, with the modifier microemulsified. Experimental data in Table XI.



TABLE XII  
Modifying Four Pairs of Monomers with Neat and Microemulsified Mercaptans

Monomers <sup>a</sup>	Ratio	Mercaptan		Pzn. rate, %/hr	<i>C<sub>tr</sub></i>	Inh. visc. $\eta$ , l./g
		<i>t</i> -C <sub>x</sub>	Added			
Bd/ACN	70/30	C <sub>12</sub>	neat	10.8	1.3	0.086
Bd/ACN	70/30	C <sub>16</sub>	neat	10.5	0.1	0.45 <sup>b</sup>
Bd/ACN	70/30	C <sub>12</sub>	ME	9.7	1.5	0.096
Bd/ACN	70/30	C <sub>16</sub>	ME <sup>c</sup>	6.9	1.4	0.14
Bd/ACN	70/30	C <sub>16</sub>	ME	8.5	1.6	0.14
Bd/EA	70/30	C <sub>12</sub>	neat	8.3	2.58	0.091
Bd/EA	70/30	C <sub>16</sub>	neat	8.3	0.28	0.45
Bd/EA	70/30	C <sub>12</sub>	ME	8.0	4.30	0.147
Bd/EA	70/30	C <sub>16</sub>	ME	7.8	4.03	0.248
St/EA	50/50	C <sub>16</sub>	neat	12.3	0.5	0.11
St/EA	50/50	C <sub>16</sub>	ME	10.1	2.3	0.048
St/EA	75/25	C <sub>16</sub>	neat	10.1	2.3	0.15
St/EA	75/25	C <sub>16</sub>	ME	14.3	2.3	0.06

<sup>a</sup> Bd = Butadiene; ACN = acrylonitrile; EA = ethyl acrylate; St = styrene.

<sup>b</sup> Contained 4% gel.

<sup>c</sup> Petroleum sulfonate surfactant, all other MEs made with Dresinate 554 surfactant.

monomer pairs. However, for all four pairs of monomer, the modification efficiency of the *t*-C<sub>16</sub> mercaptan is significantly improved by microemulsification. In case of the 70/30 butadiene-acrylonitrile pair, the microemulsified *t*-C<sub>16</sub> mercaptan approaches the neat dodecyl mercaptan in modification efficiency on a molar basis.

## DISCUSSION

### Microemulsion Preparations

The ease of forming microemulsions of mercaptans with the ingredients readily available in the emulsion polymerization industry made any extended study of microemulsion preparations unnecessary. The regulating indexes did not vary as much as might be expected with some of the variables used in preparing the microemulsions. Thus, the different alcohols and electrolytes made very little difference in the *r* value, while variable neutralization made only a 45% difference in *r* between the lowest and highest percentage neutralization of the rosin acid soap (Table III). In practical applications, however, one of the lighter alkanols might be more economical than the hexanol that was used for most of the microemulsions in this study.

Variation in amounts of petroleum sulfonate and sodium rosin surfactant had the largest effect on the regulating indexes of the modifiers. In case of *t*-C<sub>16</sub> mercaptan, the high *r* values of 10 and 12 indicated that these modifiers were inefficient as used in the SBR systems. Of much higher efficiency in the SBR system are modifiers with *r* values in the 2-6 range. Thus, control of *r* values in this range is of greatest interest. One way of controlling the regulating index of *t*-C<sub>16</sub> mercaptan was to replace part of the modifier with an inert solvent (Fig. 2). With lower mercaptans, such as C<sub>13,2</sub>, less than 5 parts of surfactant, in addition to diluent, was used to lower the regulating index below 5. With these lower amounts of surfactant, macroemulsions were formed. Although these were less stable than desired, the regulating index could be controlled by this procedure.

### Charging Microemulsions

The order and method of charging microemulsions had a much greater effect on the regulation index than is found when charging neat mercaptan in SBR systems. The order of charging neat mercaptan prior to preemulsification has essentially no effect on modification efficiency. However, for reproducible modification, the preemulsification before initiation has to be consistent.<sup>1</sup> An exception to charging order of neat mercaptan arises in the case of acrylonitrile-other monomer mixtures modified with normal mercaptans where the possibility of cyanoethylation should be minimized.<sup>14</sup> With microemulsions of modifiers, in contrast to neat mercaptan in SBR systems, the preferred way of charging is to add the microemulsion just prior to initiation (Table V). The second preferred way of charging is the addition of the microemulsion continuously below the surface of the stirred recipe soap solution. Both of these addition procedures are practical.

Incremental addition of the petroleum sulfonate-*t*-C<sub>16</sub> mercaptan micro-

emulsion was unsuccessful because the second increment added at about 30% conversion was apparently destroyed. However, this deficiency of the second increment could be overcome by first preconditioning the microemulsion by adding it to a small amount of the recipe soap solution before injecting it into the polymerization system (Fig. 4). This complication was not present when the microemulsion was made with the same surface active agent that was used in the polymerization system.

The depletion curves for the microemulsions were sometimes nonlinear, and at higher conversions the slopes tended to approach that of the neat mercaptan charged originally. These examples of instability of micro- and macroemulsion in polymerization systems suggest that the environment into which they are added has to be favorable in order that the desired reactivity and reproducibility are achieved.

### Mechanism of Modification

A tentative mechanism is proposed to account for the high rates of depletion obtained with the microemulsified modifiers. The microemulsified particle apparently maintains its identity during the course of polymerization. The modifier diffuses from its particle through the aqueous phase into the monomer-polymer particle which is the site of polymerization. The evidence supporting this proposal is as follows: (1) Kolthoff and Harris<sup>15</sup> proposed that a C<sub>12</sub> mercaptan does indeed exist in a separate particle after the monomer phase disappears; (2) an apparent relationship exists between the particle size of the microemulsion dispersed in the recipe soap solution and the regulating index, (Fig. 6, Table VII); (3) the depletion curve of the mercaptan added as a microemulsion closely parallels that of the neat mercaptan having the same regulating index (Fig. 7); (4) certain charging orders or charging procedures can result in the loss of enhanced modifier depletion which is attributed to the destruction of the microemulsified modifier particle, (Table V, Fig. 4); and (5) the environment into which the microemulsion is added can be either favorable or unfavorable, i.e., the rate of depletion can be either enhanced or retarded in comparison to a microemulsified control.

Further support of the proposed mechanism can be obtained from a consideration of the relative sizes of the particles that would be involved. Harkins reported<sup>16</sup> that the monomer particles dispersed in an SBR emulsion system have diameters of about 1  $\mu\text{m}$ . One gram of a 70/30 butadiene-styrene mixture, assuming volumes are additive, when dispersed into particles of 1  $\mu\text{m}$  in diameter had a surface area of 8.75 m<sup>2</sup>/g. Using 1- $\mu\text{m}$  diameter for monomer particles and the smallest microemulsion particle measured by light scattering photometry, one can calculate that 0.5 g of microemulsified modifier has more particles than 100 g of the monomer dispersion. The explanation for the high rates of depletion of the microemulsified modifier becomes plausible if one assumes these particle sizes and numbers are approximately correct and takes into account the concentration difference between the modifier in the microemulsion and that in the monomer particle in the control system.

Measurements of the microemulsified particle in the emulsion polymerization system is needed to establish positively the proposed mechanism. Work on this problem is planned.

### Practical Application

Experiments in this report show that the use of microemulsified modifiers in emulsion polymerization systems is more complicated than in the standard system. This is understandable when one realizes that two emulsion systems have to be prepared which also have to be compatible during the course of polymerization. However, when the proper microemulsions and charging techniques are employed, reproducible and efficient modifications with high-molecular-weight modifiers are possible.

In this exploratory phase of the research, the microemulsified dodecyl mercaptans were found more efficient than the neat modifier in only the chloroprene systems (Table XI). However, in no case was an effort made to optimize the microemulsified *t*-C<sub>12</sub> mercaptan in any of the systems. In contrast, the microemulsified *t*-hexadecyl mercaptan was much more efficient than the neat *t*-C<sub>16</sub> modifier in all six emulsion systems examined.

An effort was made to obtain a modification efficiency with microemulsified *t*-C<sub>16</sub> mercaptan as high as that obtained with *t*-C<sub>12</sub> mercaptan in the SBR 1500 control. None of the microemulsions or charging procedures of *t*-C<sub>16</sub> modifier gave as high an efficiency versus the *t*-C<sub>12</sub> control, but on a molar basis only 24% more of the microemulsified *t*-C<sub>16</sub> mercaptan was needed to obtain the same Mooney viscosity (Fig. 8, Table VIII). Nevertheless, the relatively high efficiency obtained with microemulsified *t*-C<sub>16</sub> mercaptan offers an opportunity to prepare latexes with improved odor. The lower odor of the microemulsified *t*-C<sub>16</sub> mercaptan is readily discernible in comparison to the microemulsified lower homologs.

The advantages found for the stable microemulsified modifiers in this exploratory research were (1) greatly increased reactivity of high-molecular-weight mercaptans in the emulsion system tested; (2) adjusting the reactivity of the mercaptans over a many-fold reactivity range; (3) significantly increased modification efficiency of the high-molecular-weight modifiers when the reactivity falls within an efficient range of modification; (4) efficient modification with high-molecular-weight modifiers in emulsion systems where odor is a critical specification; and (5) the addition of microemulsified high-molecular-weight mercaptans during the course of polymerization without loss of modification efficiency.

The principal disadvantage is the necessity of finding an microemulsion that is stable and compatible with the emulsion polymerization system during the major course of the polymerization. This report shows that this latter objection can be overcome in the six emulsion systems tested.

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