

Emulsion Polymerization of Butadiene and Styrene in the Presence of Carbon Black. II. Hydroperoxide Initiation

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INTRODUCTION

The first paper of this series¹ described the polymerization of butadiene and styrene in the presence of carbon black with potassium persulfate as the initiator. Although it was shown that polymerization in the presence of black is possible, nevertheless the recipe developed suffered from two major drawbacks: (1) a relatively low rate of polymerization which fell off rapidly past 50% conversion, and (2) instability of the carbon black dispersions when the conversions exceeded 30%. Both of these problems were solved when a change was made from persulfate to hydroperoxide initiation. It is the purpose of the present paper to describe the results obtained under the latter conditions and the effect of various variables upon the polymerization, and also to evaluate the polymers obtained.

EXPERIMENTAL

Two polymerization recipes were employed for most of the work described below. One, recipe A, was for the preparation of polybutadiene, while recipe B was used for butadiene-styrene systems. These recipes are given in Table I. Any deviations from these will be pointed out as necessary.

In all the bottle polymerizations the soap was handled as a solution of 62.5 g. soap per 1000 g. distilled water. These solutions were purged with nitrogen, capped, and kept in a bath at the polymerization temperature.

The carbon black dispersions were prepared by adding 63 g. of black to a Waring Blender containing 385 g. of boiled distilled water and 6.3 ml. of 1*N* NaOH. This mixture was agitated for 30 sec., and then 31.5 ml. of 10% Daxad 11 solution were added in five or six increments of about 5 ml. each. The slurry was agitated after each addition for about 30 sec., and for 5 min. after the last increment had been added. Thus prepared, the

slurry could be charged directly or stored until needed.

The sequence of charging a bottle was as follows: (1) carbon black, (2) soap solution, (3) styrene, when used, (4) butadiene, (5) modifier, and (6) initiator. Both of the latter were introduced by injection with a syringe. The bottles were then placed in a thermostat and rotated with end-over-end agitation at 28-30 rpm as before.¹

All sampling of the bottles was done with hypodermic syringes. Samples obtained were vented and then their total solids determined. Vented samples were checked against unvented ones, and the conversions obtained by the two means were in satisfactory agreement.

Polybutadiene latices were stripped for 20 min. with only jacket steam at a pressure of ca. 200 mm. Hg. Final batch temperatures were usually

TABLE I
Recipes for Polymerization in the Presence of Carbon Black

	Parts by weight	
	Recipe A	Recipe B
Butadiene	100	71
Styrene	0	29
Water (total, distilled)	180	180
OSR soap flakes ^a	5	5
Dodecyl mercaptan (DDM) ^b	0.60	0.60
Cumene hydroperoxide (CHP)	0.20 ^c	1.0 ^c
Carbon black ^d	15	15
Daxad 11 ^e	0.75	0.75
NaOH	0.06	0.06

^a Sodium soaps of fatty acids, Office of Synthetic Rubber specification.

^b Distilled fraction boiling at temperatures up to 130°C. at 5 mm. Hg.

^c Millimoles, based on actual hydroperoxide content.

^d Charged as a dispersion in water with Daxad 11 and the NaOH.

^e Polymerized sodium salts of alkyl naphthalene sulfonic acid. The amount required to disperse black varies with lots and types of black.

TABLE II
The Effect of Cumene Hydroperoxide on the Polymerization Rate of Butadiene in the Presence of Carbon Black
(15 parts Statex K; Temp. = 50°C.)

Run no.	Parts		% Conversion at hours							
	K ₂ S ₂ O ₈	CHP	1.0	2.0	3.0	4.0	5.0	6.0	12.0	14.0
C-980	0.30	0	—	6	—	—	—	—	34	41
C-982	0.30	0.10	—	22	—	—	—	—	34	39
C-991	0.20	0.10	14	—	28	—	34	—	—	—
C-993	0.10	0.10	—	34	—	42	—	55	—	—
C-1000	0	0.10	22	35	55	70	80	91	—	100 ^b
C-1001	0	0.20	25	45	65	91	100	—	—	—
C-101 ^a	0	0.20	3	9	16	31	—	44	—	100 ^b

^a Control without added carbon black.

^b These conversions may have been reached in less than 14 hr.

about 40°C. Copolymer latices were stripped initially as above, and then for one hour with both jacket steam and live steam introduced into the latex. Batch temperatures were usually 50–55°C. at 200 mm. Hg.

The latices obtained in this manner and by the methods to be described had a bluish-black appearance, and were *very stable* to both agitation and storage. In fact, a bottle of such latex kept on a shelf for several years showed no deposit, coagulum, cream, or other type of destabilization. Even so, when suitably treated with salt-acid, the latices coagulated readily to yield polymer crumb which could be readily handled and dried.

RESULTS

Effect of Cumene Hydroperoxide on Polymerization Rate

In Table II, run C-980 typifies the conversions observed with the "optimum" persulfate recipe described in the preceding paper. To see what effect cumene hydroperoxide (CHP) would have as initiator in this system, the recipe was modified both by addition of CHP and by replacement of the K₂S₂O₈ by CHP. The results obtained, given in Table II, show that the rate of polymerization is not improved by addition of CHP unless the persulfate content is reduced appreciably. When the persulfate is eliminated entirely, the rate becomes much more rapid, resulting in practically complete conversion of the butadiene to polymer in 5–6 hr. Again, comparison of run C-101, without carbon black, with run C-1001, containing black, reveals that the rate of polymerization is much higher in the presence of the black, yielding for 0.20 part CHP a conversion of 91% in 4 hr. as against 31% for the control. Further, the rate is

sustained throughout the course of the reaction, whereas the persulfate recipe gives a slowdown in rate past 50% conversion.

The latices obtained with the CHP recipe were found to be very stable and to show no separation or settling of black at any level of conversion. Again, the polymers recovered from the latices by salt-acid coagulation were nonbleeding, and contained all the carbon black originally charged.

Since the replacement of the persulfate by CHP overcame all the difficulties encountered with the persulfate recipe, a detailed study was made of the effect of a number of variables upon the polymerization rate with CHP as the initiator. The results of these studies are summarized below.

Effect of Styrene Addition

To determine the effect of styrene on the rate of polymerization of recipe A in Table I, butadiene and styrene in various ratios were run with only 0.20 part CHP as the initiator. The results obtained (Table III), show that presence of styrene has no significant effect on the polymerization rate at butadiene/styrene ratios down to 80/20. At a ratio of 70/30 the rate is actually faster. Again all the latices obtained were fluid and stable. The polymer recovered from the 70/30 latex was found to have a Mooney viscosity (ML-4) of

TABLE III
Effect of Styrene Addition on Polymerization Rate at 50°C.

Run no.	Buta- diene, parts	Sty- rene, parts	% Conversion at hours					
			1.0	2.0	3.0	4.0	5.0	6.0
C-1011	100	0	23	43	65	88	—	96
C-1012	90	10	21	39	64	88	98	100
C-1013	80	20	23	41	58	76	98	—
C-1014	70	30	27	52	87	—	—	—

TABLE IV
Effects of Various Carbon Blacks on the Polymerization Rate of Butadiene at 50°C.

Run no.	Carbon black	% Conversion at hours									
		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	16.0
C-1030	Statex K	22	61	86	95	98	—	—	—	—	—
C-1020	Statex B	18	34	46	61	78	93	100	—	—	—
C-1021	Statex R	12	29	42	60	70	86	96	100	—	—
C-1050	Philblack 0	21	32	36	43	61	85	96	—	—	—
C-1022	Micronex W-6	10	21	30	39	47	58	70	85	92	—
C-1031	Wyex	7	27	37	40	48	57	67	—	—	90
C-1023	Statex M	13	23	31	37	46	51	56	58	62	95

114; nevertheless, the polymer banded immediately on the mill and, after two minutes of milling, the stock was free of holes and smooth.

Effects of Various Carbon Blacks

Since the persulfate-catalyzed polymerization of butadiene was quite sensitive to the type of carbon black used, a study was made with recipe A to ascertain the effects of various types of carbon black on the CHP-catalyzed reaction. The results obtained are shown in Table IV. These data reveal that all the blacks used allow practically complete conversion of the butadiene to polymer, but the rate of this conversion, although higher with the CHP initiation, is still strongly dependent on the type of black used. Significantly, the order of effectiveness of the blacks is about the same as that observed with persulfate. However, with the CHP reaction total conversion is reached sooner, the reactions are smoother and more complete, and the resulting latices are more stable. It is of interest to observe that the rate of reaction can be controlled here by the type of black used, and can be made to vary so that from about 5 to 18 hr. are required for complete conversion.

The effects of the above blacks on the polymerization of butadiene at 40°C. were also observed. As a result of this 10° drop in temperature

the rates decreased, as expected, but they were still rapid enough to yield 74–88% conversions in 7 hr. for the first four blacks listed in Table IV. On the other hand, the remaining blacks gave conversions of only 31–46% in the same period of time.

Effect of Rosin Soap

In Table V are given results obtained with recipe A when the 5 parts SF flakes were replaced with an equal number of parts of a rosin soap, namely, the sodium soap of Resin 731 or Dresinate 731. These data show that substitution of Dresinate 731 for the fatty acid soap leads to a considerable reduction in polymerization rate. Further, the effects of the different blacks are less pronounced in all cases except that of Wyex, where the reaction seems to have stopped at a conversion of ca. 25%.

Effect of Soap Mixtures

Recipe A with 15 parts Statex K and 5 parts SF flakes gives complete conversion of butadiene to polymer in about five hours. Within the same time period the same recipe with 5 parts of Dresinate 731 gives a conversion of about 25%. To ascertain the effect of mixtures of the two soaps, runs were made employing 5 parts of soap composed

TABLE V
Effect of Rosin Soap on Polymerization of Butadiene in the Presence of Various Carbon Blacks at 50°C.^a

Run no.	Carbon black	% Conversion at hours							
		1.0	2.0	5.0	7.0	9.0	17.5	24.0	
C-1032	Statex K	5	13	23	35	—	65	—	
C-1033	Statex B	5	10	20	—	36	63	82	
C-1034	Statex R	4	15	24	—	37	60	72	
C-1035	Statex M	4	14	25	—	49	61	—	
C-1036	Micronex W-6	2	6	12	—	42	—	—	
C-1037	Wyex	1	10	11	17	—	25	24	

^a In these runs 5 parts Dresinate 731 replaced an equal weight of SF flakes.

TABLE VI
Effect of Carbon Black Loading on Polymerization of Butadiene at 50°C.

Run no.	Parts Statex K	% Conversion at hours						State of latex
		1.0	2.0	3.0	4.0	5.0	6.0	
C-1060	1	14	24	30	—	62	65	Fluid, no coagulum
C-1061	5	17	37	57	64	—	100	"
C-103	15	22	61	86	95	98	—	"
C-1120	20	25	33	40	62	80	80	"
C-1121	25	26	35	40	63	73	73	"
C-1122	30	25	48	72	75	78	—	"
C-1123	35	23	45	59	58	49	—	Large amounts of coagulum
C-106	40 ^a	1	11	20	—	29	31	"
C-104	50 ^a	19	36	43	50	50	58	"

^a Runs C-106 and C-104 contained, respectively, 220 and 250 parts of water.

^b Conversions for the last three runs are meaningless because of the coagulum formation, and were larger than shown by the data since all bottles "pressure dropped."

of various proportions of the two. The times of reaction were found to be intermediate between the above limits, with no appreciable improvement in rate occurring until the ratio of SF flakes to rosin soap contents was at least 4:1. Even then, however, the conversion after 5 hr. was only 55%, in contrast to the complete conversion obtained with 5 parts SF flakes. Therefore, mixtures of the two soaps offer no advantage unless a slowdown in the reaction rate is sought.

Effect of Carbon Black Loading

To determine the effect of carbon black loading on the rate of the CHP-catalyzed polymerization and on the stability of the resulting latices, a series of runs was made with recipe A in which the amount of Statex K was varied from 1 to 50 parts per 100 parts of butadiene. The amounts of of Daxad 11 and NaOH required for these loadings varied with the charge, but in all cases they were 5% and 0.4%, respectively, of the parts black used. The results of these runs, shown in Table VI, indicate that reasonable conversions are obtainable at all carbon black loadings employed. However, they also show that there is an optimum black loading for a given soap and catalyst con-

centration. For the conditions employed, i.e., for Statex K with 5 parts SF flakes and 0.20 part CHP, the fastest rate was observed at 15 parts black. At loadings above 30 parts the amount of soap present was insufficient to stabilize the system, and hence coagulum resulted. At the other extreme, the one part of black present in run C-1060 was not enough to make any significant contribution to the reaction rate. In any case, the results show that recipe A can be used satisfactorily in the presence of up to 30 parts of carbon black loading. With emulsifier and initiator adjustment the black loading could be increased to even higher levels.

Effect of Soap Content

In Table VII are given data obtained in a series of runs in which the charge of SF flakes was varied between 2 and 5 parts per 100 parts monomer. In all cases 15 parts Statex K was used along with 0.20 part CHP.

The major effect resulting from reduction of the soap content is a decrease in polymerization rate. Five parts of soap yields a conversion of 98% in 6 hr., and the rate falls progressively with soap content until at 2 parts soap the conversion is

TABLE VII
Effect of Soap Content on Polymerization of Butadiene at 50°C.

Run no.	SF flakes, parts	% Conversion at hours						State of latex
		1.0	3.0	5.0	6.0	8.0	10.0	
C-1051	2.0	6	10	14	16	—	22	Fluid with coagulum
C-1052	3.0	12	18	22	26	36	42	Fluid, no coagulum
C-1053	4.0	14	24	35	42	56	70	"
C-104	5.0	21	60	94	98	—	—	"

only 16% in the same time. Further, 3 parts of soap appears to be sufficient to keep both the polymer and black dispersed, whereas 2 parts of soap is insufficient to do so.

Effect of Storing Carbon Black Slurry

Various experiments were made to ascertain whether the carbon black slurries prepared for polymerization must be used directly, or whether they can be prepared and stored until needed. The results of these runs showed that the black slurries can be stored for days either alone or mixed with the soap solution without effect on either the polymerization rate or the stability of the latices.

Effect of Carbon Black Slurry Preparation

Since the combination of CHP and carbon black was found to be responsible for the rapid polymerization rates reported here, it was expected that the degree of dispersion of the black in the slurry would be an important rate-determining factor. To test this point, five methods of slurry preparation were tried and their effect on the rate determined. The methods employed are listed in Table VIII, along with data obtained on the polymerization of butadiene (recipe A) at 50°C.

with the corresponding slurries. These results show definitely that the mechanical method employed for preparing the carbon black dispersions is one of the most important factors in determining the polymerization rate. If rate can be used as an index of the quality of the dispersion, then the effectiveness of the means of dispersion decreases in the following order: Waring Blendor, homogenizer, ball mill, malted milk shaker, and shaking by hand. It is also obvious from these results that reproducibility and reliability of the polymerization rates require that a standardized method be used for the carbon black slurry preparation. In our case the standardized procedure used was that described in the experimental section. As the results of Table VIII show, that procedure is the best of the methods tried.

The carbon black slurries employed in the polymerizations described thus far all contained Daxad 11 as the dispersing agent. To ascertain the effect of other agents on the rate of polymerization and the stability of the resulting latices, a series of runs was made with recipe A in which the emulsifier was varied as indicated in Table IX. In instances where emulsifier was used, the quantity employed was that needed to obtain a fluid carbon black dispersion with the Waring Blendor. The use of all four dispersing agents shown

TABLE VIII
Effect of Method of Dispersing Black on the Polymerization of Butadiene at 50°C.

Run no.	Dispersion method	% Conversion at hours					
		1.0	2.0	3.0	4.0	5.0	6.0
C-1340	Waring Blendor	26	50	77	90	—	—
C-1341	Malted milk shaker	21	31	38	50	68	82
C-1342	Ball mill	15	33	49	62	66	69
C-1343	Homogenizer	14	35	57	80	90	—
C-1344	Shaking by hand	3	24	26	28	29	29

TABLE IX
Effect of Various Carbon Black Dispersing Agents on the Polymerization of Butadiene at 50°C.

Run no.	Statex K, parts	Dispersing agent	% Conversion at hours					
			1.0	3.0	5.0	6.0	7.0	17.0
C-1070	5	None	11	24	45	56	65	92
C-1071	15	None	8	14	25	34	41	66
C-1080	15	Daxad 11	23	69	82	87	—	—
C-1081	15	Triton R-100 ^a	22	31	79	92	—	—
C-1082	15	Marasperse CB ^b	23	48	71	75	79	—
C-1083	15	Indulin A ^c	20	52	82	83	—	—

^a Neutral sodium salts of complex condensed organic acids.

^b Partially desulfonated sodium lignosulfonate.

^c Purified pine wood lignin.

TABLE X
Effect of Hydroperoxides and Peroxides on the Polymerization of Butadiene at 50°C

Run no.	Catalyst	% Conversion at hours					
		1.0	3.0	5.0	6.0	7.0	9.0
C-1040	Cumene hydroperoxide	21	60	94	98	—	—
C-1041	Diisopropylbenzene hydroperoxide	24	74	97	100	—	—
C-1042	<i>p</i> -menthane hydroperoxide	18	58	91	95	96	—
C-1043	<i>tert</i> -Butyl hydroperoxide	10	32	54	64	74	90
C-1044	Di- <i>tert</i> -butyl peroxide	0	0	0	—	—	0
C-1045	Benzoyl peroxide	0	4	—	10	—	—

in the table resulted in good conversions in six hours, the highest conversions being obtained with Daxad 11 and Triton R-100. In absence of any black dispersing agent the rate of polymerization was lowered, particularly where 15 parts black was used, and the latices obtained showed carbon black separation. On the other hand, all latices prepared in the presence of dispersing agent were uniformly fluid, well dispersed, and stable.

Effect of Hydroperoxides and Peroxides

Several hydroperoxides and peroxides were tested for comparison of their activity to that of CHP. In all runs 1.0 mmole of initiator, 15 parts of Statex K, and 5 parts of SF flakes were used. The polymerization data obtained are given in Table X, where it may be seen that the hydroperoxides having cyclic structures all showed about the same degree of activity, and that their use resulted in the highest rates. On the other hand, the two peroxides exhibited little or no activity. With the one aliphatic hydroperoxide tested, *tert*-butyl hydroperoxide, a rate was obtained which is fairly high, but still lower than that

given by the cyclic hydroperoxides. Therefore, it appears that for the system described, polymerization in the presence of carbon black can be initiated effectively with hydroperoxides, but that the peroxides tested are either negligibly or only mildly effective. This observation accounts for the relatively poor results obtained with the persulfate recipe described in the preceding paper.

Effect of Modifiers

In all the runs described thus far dodecyl mercaptan (DDM) was used as the modifier. To determine the effects of other modifiers on the rate of polymerization of butadiene at 50°C., two other commercial modifiers, namely, Sulfole (*tert*-dodecyl mercaptan) and MTM-4 (a mixture of C₁₂, C₁₄, and C₁₆ tertiary mercaptans), were used in place of DDM, also in 0.60 pph concentrations. All three mercaptan modifiers were found to act identically when used in recipe A, and to yield 100% conversions in 5-hr.

Commercially obtainable DDM is a mixture of products whose boiling points range from below 120°C. to above 175°C. at 5 mm. Hg pressure. To ascertain whether all fractions of this product

TABLE XI
Activities of Various Fractions of DDM in Polymerization of Butadiene at 50°C.

Run no.	Mercaptan	% Conversion at hours			
		1.0	3.0	5.0	8.0
C-1370	DDM as received	14	44	77	93
C-1371	Fraction boiling below 121°C. ^a	18	65	92	94
C-1372	Fraction boiling 121–131°C.	12	44	77	90
C-1373	Fraction boiling 131–141°C.	0	0	—	23
C-1374	Fraction boiling 141–151°C.	0	5	—	15
C-1375	Fraction boiling 151–173°C.	0	4	—	16
C-1376	Still pot residue	0	5	—	8
C-1377	None	2	—	10	10

^a All boiling ranges were measured at 5 mm. Hg.

possess equal activity with regard to rate, the product "as received" was fractionated and the fractions were tested at 0.60 part levels in recipe A. The results obtained are given in Table XI. These data show that the original product and the fractions boiling below 131°C. possess nearly equal and relatively high rate activity. The higher fractions show much lower activity, and the highest boiling fractions almost none. Hence the active portion of the DDM is the fraction boiling below ca. 130°C. at 5 mm. Hg. This portion constitutes about 75% of the total, the remainder being rather inert in recipe A. Therefore, in order to use only active ingredients in the present study, the DDM fraction boiling at temperatures up to 130°C. at 5 mm. Hg was employed.

Effects of Iron and Oxygen

Since trace quantities of iron are frequently responsible for variations in the rates of polymerization of some recipes, the effects of small amounts of ferrous iron on recipe A were investigated. The quantities of iron added were 0.1, 1.0, and 10.0 ppm relative to the total charge weight. The first two additions produced no effect. The 10.0 ppm charge caused a slight retardation in rate, but a conversion of 82% was still obtained in 8 hr.

Since carbon black possesses a large adsorptive surface area, one may expect to encounter difficulties in making surfaces oxygen-free by ordinary purging techniques. For this reason it was decided to employ a chemical scavenger for the removal of adsorbed oxygen, and thus to ascertain whether surface oxygen affects the reaction rate. The substance used for this purpose was $\text{Na}_2\text{S}_2\text{O}_4$, which was injected after all ingredients except CHP were charged. The charge was then rotated at 50°C. for 15 min., after which the CHP was added. The results obtained after treatment of the charges with 0.0023–0.115 mmoles of $\text{Na}_2\text{S}_2\text{O}_4$ were identical with those obtained without such treatment. This fact suggested that the recipe may be insensitive to oxygen. To test the latter point, two series of charges, based on recipes A and B, were deliberately contaminated with molecular oxygen and their polymerization behavior was observed. The results are presented in Table XII.

From the data in this table it is evident that both recipe A and recipe B are insensitive to oxygen. If anything, it is shown in control run C-1335 that oxygen in the system may promote

TABLE XII
Effect of Molecular Oxygen on the Polymerization of Butadiene, and Butadiene and Styrene, at 50°C.

Run no.	O_2 , mmole/- 100 g. monomer	% Conversion at hours				
		1.0	2.0	3.0	4.0	6.0
Polymerization of Butadiene						
C-1330	(^a)	15	30	44	63	88
C-1331	0.027	16	31	47	64	88
C-1332	0.053	17	31	49	66	90
C-1333	0.133	12	29	38	68	88
C-1334	0.267	16	30	42	—	86
C-1335	(^b)	27	54	78	—	92
Copolymerization of Butadiene and Styrene						
C-1270	0.025	22	43	56	81	93
C-1271	0.050	24	42	57	81	93
C-1272	0.125	23	41	58	80	90
C-1273	0.250	21	41	55	76	93

^a Control; charged as described in Experimental section.

^b Control; neither soap solution nor carbon black slurry was prepared with distilled water, and all operations were conducted in air without subsequent nitrogen purging.

higher reaction rates, and that no precautions for excluding oxygen, such as nitrogen purging, are necessary.

Physical Properties of Styrene-Butadiene of Copolymers

A series of 5-gallon runs was made at 50°C. to obtain polymer for the evaluation of physical properties. In these runs recipe B was used throughout with 15 parts Statex R and 0.15 part initiator on a pure CHP basis. Further, in order

TABLE XIII
Butadiene-Styrene Copolymerization in 5-Gallon Reactors at 50°C.

Run no.	DDM, parts by weight	Conversion, %	Time, hr.	Black in polymer, parts by weight	Mooney viscosity (ML-4)
5-21	0.60	68	2.2	22.0	168
5-23	0.60	68	2.0	22.0	152
5-24	0.60	71	1.9	21.2	143
5-25	0.60	70	1.9	21.4	166
5-26	0.60	68	2.0	22.0	141
5-27	0.60	68	2.2	22.0	127
5-28	0.65	70	2.2	21.4	123
5-29	0.55	74	2.6	20.2	129
5-30	0.50	72	2.5	20.8	147

TABLE XIV

	Parts by weight
Polymer	100
Carbon black	40
Softener (BRT No. 7)	5
Zinc oxide	5
Sulfur	2
Altax	1.75

to compare the product with standard butadiene-styrene rubber prepared at 50°C. with persulfate initiator and in absence of carbon black, the conversions were kept to about 70%, the conversion used in the preparation of GR-S rubber.

Table XIII gives the polymerization data for these 5-gallon runs, and shows that conversions of 68-74% were attained in 1.9-2.6 hr. The resulting latices, after venting and stripping, were in all cases very fluid, and showed no tendency to

settle even though they contained 20-22 parts black per 100 parts polymer. They coagulated readily and cleanly with salt and sulfuric acid to yield crumbs which were washed and dried to non-bleeding polymer. Standard Mooney viscosity tests (ML-4) run on these polymers gave the results shown in the last column of Table XIII. The viscosities are much higher than the Mooney values near 50 which are specified for all standard GR-S rubbers.

Prior to curing and testing, the polymers listed in Table XIII were compounded according to the formula shown in Table XIV.

The additional carbon black required to bring the black content up to 40 parts was introduced on the mill. No difficulty of any kind was experienced during the compounding, even though the Mooney viscosities of the polymers were very high. In fact, the polymers banded readily and smoothly on the mill. After two minutes of

TABLE XV
Physical Properties of Butadiene-Styrene Copolymers Prepared in the Presence of Carbon Black at 50°C.

Run no.	Mooney viscosity (ML-4) of compounded polymer	Cure time, min.	200% Modulus, psi	300% Modulus, psi	Ultimate tensile strength, psi	Ultimate elongation, %
5-21	82	15	240	420	3210	800
		30	460	800	4130*	650*
		45	520	1130	3980	590
5-23	76	15	180	270	1870	930
		30	290	550	3820	770
		45	380	750	4840*	710*
5-24	72	15	240	400	2450	830
		30	430	970	4220*	680*
		45	640	1410	4000	560
5-25	88	15	290	500	3000	760
		30	530	1100	4120*	610*
		45	700	1580	3860	530
5-26	70	15	340	480	3880	760
		30	590	1160	4250*	620*
		45	700	1520	3890	550
5-27	60	15	230	420	3310	850
		30	400	760	4060*	700*
		45	480	1030	3440	570
5-28	61	15	260	450	3290	810
		30	460	830	4020*	670*
		45	560	1190	3820	590
5-29	67	15	210	340	2380	830
		30	430	960	3950*	660*
		45	580	1240	3670	550
5-30	75	15	240	380	2680	820
		30	470	930	4090*	670*
		45	550	1180	3710	540

* Values used in calculating the average ultimate tensile strength, 4130 psi, and the average ultimate elongation, 660%.

milling the banded stocks were free of holes and absorbed the additional black easily and quickly. These observations show that the polymers prepared in the presence of carbon black may be processed readily even at high Mooney viscosities, whereas this is not true of polymers prepared in the absence of black.

After compounding, the polymers were cured at 145°C. The physical test data obtained on these cured stocks are summarized in Table XV. These show for the polymers an average ultimate tensile strength of 4130 psi and an ultimate elongation of 660%. This tensile strength is considerably superior to that shown by GR-S rubbers even at a loading of 50 parts black.

CONCLUSIONS

Results given in the present paper definitely show that both butadiene and butadiene and styrene can be emulsion polymerized and copolymerized smoothly and rapidly in the presence of carbon black when the reactions are initiated by hydroperoxides such as those of cumene, diisopropylbenzene, or *p*-menthane. These hydroperoxides yield, in the presence of 15 parts of carbon black, 100% conversions in 5 to 6 hr. Further, the recipes are insensitive to oxygen or to appreciable quantities of ferrous iron, but they are strongly affected by the preparation of the carbon black dispersions prior to polymerization.

The latices resulting from the polymerizations have been found to be very fluid and colloidal stable, showing no tendency, over very long periods of time, of either the black or polymer to separate from the dispersion. Nevertheless, the latices are readily coagulated with salt-acid and yield, on precipitation, nonbleeding crumb which is readily dried.

The polymers prepared in the presence of carbon and with cumene hydroperoxide as initiator possess, by ordinary standards, very high Mooney viscosities. Still, they are readily processed; they band easily on a mill and absorb additional black very rapidly. In these respects they are very different from ordinary butadiene-styrene rubbers of high Mooney viscosity. Further, butadiene-styrene polymers prepared at 70% conversion in the presence of 15 parts black, and compounded with additional carbon black up to 40 parts, give ultimate tensile strengths of about 4100 psi and ultimate elongations of 660%. These

tensile strengths are considerably higher than those given by 71/29 butadiene-styrene rubbers prepared at 50°C. by the persulfate recipe and in absence of carbon black.

Reference

1. Maron, S. H., W. von Fischer, W. M. Ellslager, and G. Sarvadi, *J. Polymer Sci.*, **19**, 29 (1956).

Synopsis

Butadiene, and butadiene and styrene, can be emulsion polymerized and copolymerized smoothly and rapidly in the presence of carbon black when the initiator is hydroperoxide rather than persulfate. With 15 parts of black per 100 parts monomer the recipe developed yields 100% conversion in 5-6 hr. and it is insensitive to either molecular oxygen or appreciable quantities of ferrous iron. However, it is strongly dependent on the method employed for dispersion of the carbon black prior to polymerization. The latices obtained are very fluid and stable, showing no tendency either to cream or to settle. Nevertheless, they coagulate readily and cleanly with salt-acid to yield nonbleeding polymers containing all the black charged. The Mooney viscosities of the polymers are very high, ranging from 120 to 170. In spite of this, the rubbers mill easily and smoothly, and they rapidly absorb on a mill any additional carbon black to be incorporated. Butadiene-styrene copolymers, prepared at 50°C. by reaction to 70% conversion in the presence of 15 parts of black and compounded to 40 parts carbon black per 100 parts polymer, have been found to yield ultimate tensile strengths of about 4100 psi at 660% elongation. These tensile strengths are superior to those shown by comparable rubbers prepared at 50°C. in the absence of carbon black.

Résumé

Le butadiène et les styrène-butadiène peuvent être polymérisés en émulsion lentement et rapidement en présence de noir de carbone quand le système initiateur est un hydroperoxyde au lieu de persulfate. Avec 15 parties de noir pour 100 parties de monomère, on obtient 100% de conversion en 5-6 heures et cela est insensible à l'oxygène moléculaire et à des quantités appréciables de fer ferreux. Cependant, cela dépend fortement de la méthode employée pour la dispersion du noir de carbone pendant la polymérisation. Le produit obtenu est très fluide et stable et il n'a aucune tendance à se prendre en crème ou en masse. Cependant il se coagule rapidement et proprement en présence d'une solution de sel acide pour donner des polymères non fluides contenant tout le noir. Les viscosités (Mooney) des polymères sont fort élevées, dans l'ordre de 120-170. Néanmoins les caoutchoucs peuvent être facilement et lentement laminés et ils absorbent rapidement par calendrage une quantité supplémentaire de noir de carbone. Les copolymères butadiène-styrène, préparés à 50°C. jusqu'à une conversion de 70% en présence de 15 parties de noir et composés de 40 parties de noir de carbone par 100 parties de polymère, forment des caoutchoucs de 4100 psi à 660% d'élongation. Ces élastomères sont supérieurs aux caoutchoucs préparés à 50°C. en absence de noir de carbone.

Zusammenfassung

Die Emulsionspolymerisation von Butadien und Butadien-Styrol kann glatt und rasch in Gegenwart von Russ durchgeführt werden, wenn zum Start Hydroperoxyde an Stelle von Persulfat verwendet werden. Mit 15 Teilen Russ auf 100 Teile Monomeres liefert das entwickelte Rezept 100% Umsatz in 5,6 Stunden und ist sowohl gegen molekularen Sauerstoff als auch gegen beträchtliche Mengen Ferroeisen unempfindlich. Es besteht jedoch eine starke Abhängigkeit von der zur Uerteilung des Russes vor der Polymerisation verwendeten Methode. Die erhaltenen Latices sind leichtflüssig und stabil und besitzen keine Tendenz zum Aufrahmen oder Absetzen. Sie koagulieren mit Salz und Säure

leicht und vollständig unter Bildung nicht auslaufender Polymerer, die den gesamten, eingebrachten Russ enthalten. Die Mooney-Viskosität der Polymeren ist sehr hoch und zwar im Bereich von 120-170. Trotzdem lässt sich der Kautschuk leicht und glatt walzen und nimmt auf einem Walzwerk rasch noch weiteren zugesetzten Russ auf. Butadien-Styrolcopolymere, die bei 50°C mit 70% igem Umsatz in Gegenwart von 15 Teilen Russ dargestellt und zu Mischungen mit 40 Teilen Russ auf 100 Teile Polymeres verarbeitet wurden, ergaben eine Reissfestigkeit von 4100 p.s.i. bei 660% Dehnung. Diese Festigkeit ist derjenigen von vergleichbaren Kautschuken, die bei 50°C in Abwesenheit von Russ hergestellt wurden, überlegen.

Received November 17, 1960