Important Quality Factors in Styrene-Butadiene Rubber (SBR) as Affected by Stabilizers and Flocculation Techniques

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In common with other unsaturated hydrocarbon materials, uncured styrene-butadiene rubber (SBR) is susceptible to oxidative degradation unless the polymer is protected from oxygen attack (*6, 8, 11*). Destructive changes which take place slowly in the raw polymer at room temperature are greatly accelerated at the elevated drying temperatures in the polymer manufacturing plant. Standard practice is to incorporate a small proportion (1.25%) of a stabilizing agent into the SBR latex prior to flocculation and drying of the polymer. Chemicals most commonly used as commercial SBR stabilizers include certain aromatic amine derivatives, phenolic compounds, and aromatic esters of phosphorous acid. The aromatic amines stain to a greater or lesser degree, whereas the phenolics and phosphorous acid esters are generally classed as nonstaining types. These materials vary considerably in their effects (*8, 18, 19*). The more highly effective stabilizers afford good protection during polymer manufacture and are beneficial in preserving the optimum quality of the polymer during subsequent hot processing operations.

Factors other than the stabilizing agent can also affect the stability behavior of the polymer, and the method of coagulating the latex has an important influence. Glasgow and Vila (*5*) demonstrated that SBR flocculated with salt and sulfuric acid exhibits poorer heat stability than polymer flocculated with sulfuric acid alone. The straight acid coagulation method is made commercially practical by using a small quantity of glue in the acid solution (*9, 10*). Alum-coagulated polymers also show improved heat stability when compared to polymer coagulated by the conventional salt-acid method (*1, 5, 15, 17, 22*). Albert and co-workers have shown that the stability of alum coagulated polymers can be related to the amount of iron impurity present in the alum flocculant (*1*). Others have also observed that iron promotes the breakdown of SBR polymers (*3, 4, 11, 16, 17*). Degradation in the presence of iron is especially pronounced when the polymer is extended with oil (*12, 13*). An enlightening discussion of the effects of organic-soluble iron in the degradation of oil-extended cold SBR is given by Reynolds (*13*). Manganese in SBR is also deleterious (*10, 14*). Surprisingly, copper has been reported to inhibit oxidation in uncured SBR polymer but to promote oxidation of an SBR vulcanizate (*15*).

SIGNIFICANCE OF SBR POLYMER STABILITY

The need for an effective stabilizer in SBR polymer first becomes apparent in the polymer manufacturing plant. The heat of the drying oven may promote resinification and discoloration of unprotected polymer. Initial melting may be followed by embrittlement and the formation of insoluble gel structure in the polymer. Such changes produce fluctuations in Mooney viscosity and gel measurements on the raw polymer and may damage the physical properties of cured vulcanizates.

The importance of protecting SBR polymer from the deleterious effects of processing heat probably deserves more serious consideration than has sometimes been given. Hot milling operations produce adverse effects upon inadequately protected polymer which appear as degraded physical properties in subsequent vulcanizates. These effects become more important as the industry increases production rates and raises processing temperatures.

Although it may be considered that the primary function of an SBR stabilizer is to protect the polymer during manufacture and processing operations, effective SBR stabilizers also benefit the aging of cured vulcanizates.

EFFECT OF HOT BANBURY MASTICATION ON SBR POLYMER

An example of the effects of processing heat on SBR properties is found in a study by Carlton of J. M. Huber Corp. (*2*) who measured the effects of hot Banbury mastication on gel formation in SBR polymer. In that study, SBR polymer was masticated at 350° F., and samples were removed at 3-minute intervals for Mooney and gel determinations. The samples were subsequently passed three times through a cold mill and the gel content measured once again. The data obtained are reproduced in Table I. Increase in mastication time lowered the viscosity and increased gel. Remilling on the cold mill redispersed the gel initially formed at the shorter mastication times but was only partially effective when the mastication time exceeded 6 minutes. The remilling technique has been utilized by White and others (*21*) as a means of classifying gel in SBR technology as "loose gel" and "tight gel."

The Huber study was extended to measuring the effects of mastication temperature on gel formation (Table II). No gel

Table I. Effect of 350° F. Banbury Mastication on Gel Formation

Time, Min.	Mooney	% Gel	% Gel (Remilled)[a]
3	55	0	0
6	52	12	0
9	47	24	20
12	36	34	30

[a] 3 passes through cold mill.

Table II. Effect of Mastication Temperature on Gel Formation

(12 min. Banbury mixing at temperature indicated)

Mastication Temp., °F.	Mooney	% Gel	% Gel (Remilled)
225	43	0	0
250	44	0	0
275	39	0	0
300	45	0	0
325	48	23	0
350	54	34	25
375	42	41	40

was detected when the polymer was masticated in the Banbury for 12 minutes at temperatures up to 300° F. At 350° and 370° F., a substantial amount of tight gel was produced which was not redispersed by passing through a cold mill.

The same investigation included the effects of gel on the cured properties of a tread stock. Vulcanizates prepared from polymers masticated in the Banbury at temperatures ranging from 225° to 375° F. gave the physical properties shown in Table III. The 200% modulus of the vulcanizates increases with increasing mastication temperature. Although no gel was detected in the polymer milled at temperatures under 325° F., the subtle effects of increasingly severe heat treatment are clearly evident in increasing modulus and in a decrease in tensile, elongation, and crack growth resistance. The adverse effects of gel are especially evident in the greatly reduced crack growth resistance of vulcanizates from polymers masticated at temperatures in excess of 300° F. The observed effects of processing heat on the physical properties of SBR vulcanizates emphasize the importance of adequate polymer stability.

Table III. Effect of Gel on Properties of a Tread Stock

Mastication Temp., °F.	% Gel	Modulus, 200%	Tensile	Elongation	Mooney	Demattia Flexing[a]
225	0	1030	4320	510	67	39,000
250	0	1040	4230	500	67	35,000
275	0	1060	4120	480	63	34,000
300	0	1130	4040	457	60	25,000
325	25	1410	3980	405	72	7,000
350	42	1700	3640	380	84	4,500
375	50	1740	3300	305	?	3,500

[a] Flexes to produce 0.5 inch cut growth.

In the present investigation, the effects of sodium chloride (as a coagulant) upon the heat stability of SBR, and the relation between polymer instability and the ultimate quality of SBR vulcanizates have been studied. Sodium chloride is employed as a flocculant in over 90% of the total SBR production. Other factors relating to the stability of uncured SBR polymer have also been examined.

EFFECTS OF VARYING AMOUNTS OF SODIUM CHLORIDE

A commercial, cold SBR latex (1503 type) made on a sulfoxylate–diisopropyl benzene hydroperoxide system and shortstopped with sodium dimethyl dithiocarbamate was treated with aqueous emulsions of commercial SBR stabilizers (1.25 parts per 100 of polymer). The latex was creamed with varying proportions of 10% sodium chloride solution and added to a well stirred solution of dilute sulfuric acid (at 60° C.) containing a small amount of glue. The salt usage was equivalent to 0, 4, 8, 10, 15, and 19 parts per 100 parts of polymer. The acid and glue in each case was equivalent to 8 parts of 100% sulfuric acid and 0.15 part of glue per 100 parts of polymer. The resulting crumb slurry was stirred until the serum was clear. The serum was drained off, and the flocculated crumb reslurried four times in fresh warm water. The polymer was squeezed to remove excess water, divided into small pieces by hand, and dried in a circulating air oven at 60° C. for 16 to 20 hours. The dried crumb was massed on a cold mill and sheeted out to 3/16-inch thickness (after shrinkage). Portions were placed in a 130° C. oven for varying periods of time. The effects of 130° C. heat on the polymer stabilized with tris (nonylated aryl) phosphite and flocculated with varying amounts of salt are shown in Table IV.

The melted appearance of the samples to the left and bottom of this section of the chart (under the diagonal line) reveals the poor heat stability of the polymer flocculated with the higher amounts of salt. As the quantity of salt used in the flocculation of the latex is decreased, the time for resinification at the 130° C. temperature increases. Those polymers flocculated with the higher amounts of salt show the poorest heat stability. Common usage of salt in commercial SBR production generally approaches the higher proportions indicated (15 to 20 parts per 100 of polymer).

Results of similar experiments with SBR 1503 stabilized with styrenated phenol, a higher alkylated phenol, and a diarylamine type stabilizer (BLE) are indicated in Tables IV and V. The samples below the diagonal line were resinified, whereas those above were in good condition. The adverse effect of sodium chloride is observed with each of the stabilizers examined. In Table V are shown the results of experiments with SBR 1503 containing no stabilizer. This polymer was carefully dried at low temperature (40° C.) to avoid resinification which will otherwise occur with unstabilized polymer at higher drying temperatures. The "salt effect" is also observed in the absence of stabilizer.

Examination of Tables IV and V and Figure 1 reveal considerable variation in the times required for resinification at any given salt level for the stabilizers tested. The decreasing effectiveness of each of the stabilizers with increasing salt usage is evident. Tris (nonylated aryl) phosphite gives most effective protection among the nonstaining stabilizers. At high salt levels, the efficiency of each of the materials is low.

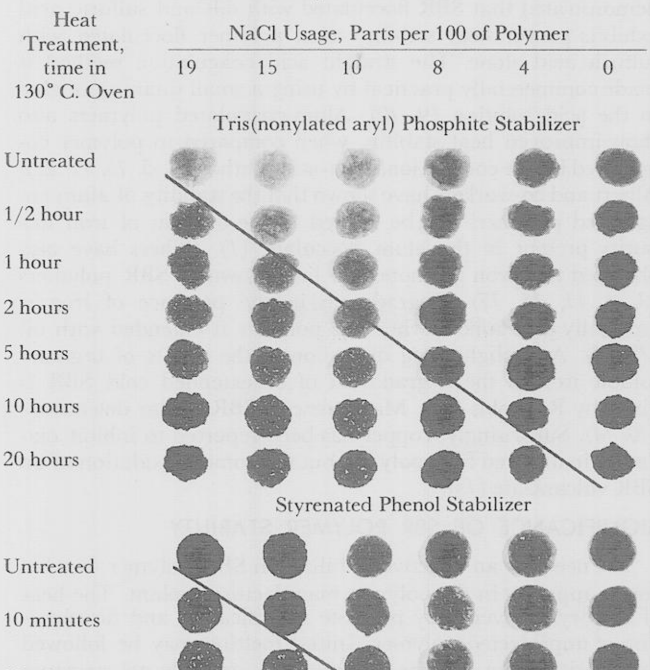
Differences between conditions of laboratory and commercial plant flocculations do not permit absolute comparisons to be made. Other studies have shown a greater advantage for the better stabilizers at the 15 to 20 parts of salt level than is indicated in Figure 1.

However, less effectively stabilized polymers are barely adequate in commercial production, and special drying precautions are usually necessary to retain good color and freedom from resinification.

EFFECTS OF POLYMER STABILITY ON QUALITY OF SBR VULCANIZATES

Two commercial "hot" SBR polymers, SBR-1000 and SBR-1007 (Synpol 1000 and Synpol 1007, Texas-U. S. Chemical

Table IV. Effects of Salt-Acid Flocculation on Heat Stability of SBR 1503



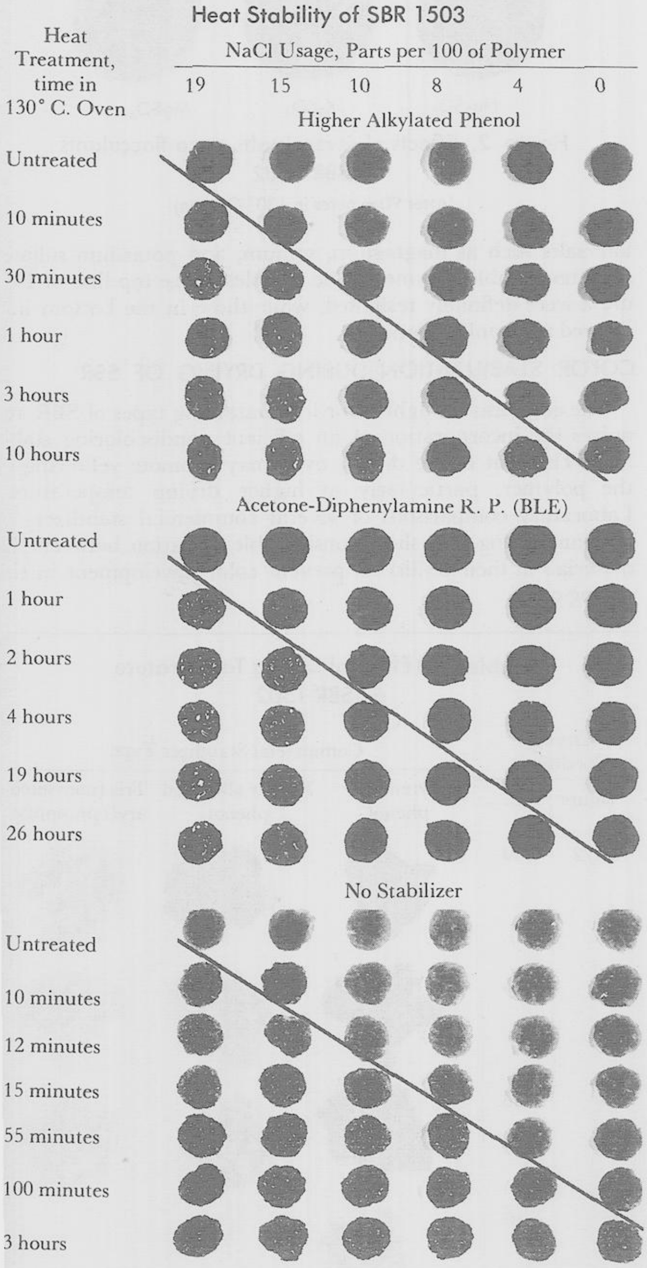
Co.), were chosen as polymers identical in all respects except that SBR-1000 is flocculated with acid and glue. The stability of the two polymers under two conditions of hot milling (15 minutes at 300° F. and 15 minutes at 350° F.) is revealed in Mooney viscosity and gel measurements on the milled polymers (Table VI).

The polymers subjected to these milling conditions were compounded and cured. The recipe is SBR-1000 (or 1007), 100.0 parts; Protox 166, 5.0; Wyex black, 40.0; sulfur, 2.0; MBTS, 1.75.

The stocks were cured for 30, 60, and 90 minutes at 45 p.s.i. (gage steam pressure at 292° F.). The unaged physical properties of the vulcanizates cured for 60 minutes at 45 p.s.i. are shown in Table VII.

Differences in the physical properties of the polymers not subjected to hot milling are not great. In those vulcanizates from polymers subjected to 300° and 350° F. milling, the effects of polymer stability become apparent. The retention of modulus, tensile, and elongation is definitely superior in the vulcanizates from the acid-glue flocculated polymer as compared to the vulcanizates from the salt-acid polymer. Similar advantages are seen in the cut growth properties of the acid-glue polymer. These data reflect the improved heat stability of the polymer flocculated without salt.

Table V. Effects of Salt-Acid Flocculation on Heat Stability of SBR 1503



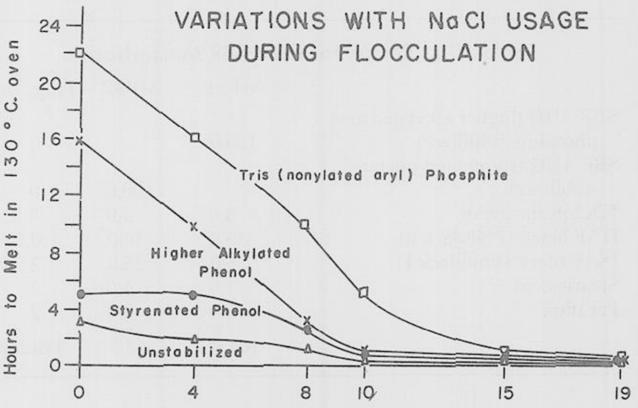


Figure 1. Relative effects of stabilizers on resinification of SBR 1503

EFFECT OF CARBON BLACK ON HOT MILL STABILITY

In experiments in which carbon black was added prior to the hot milling treatment to SBR-1000 and SBR-1007, the differences in the vulcanizates from the salt-acid and the acid-glue flocculated polymers were much less apparent than when the polymers were hot milled in the absence of carbon black (*20*). However, in a similar study, in which two commercial "cold" SBR polymers stabilized with styrenated phenol and with higher alkylated aryl phosphite, respectively, were hot milled for 15 minutes at 340° F. in the presence of carbon black, the more adequately stabilized polymer exhibited definite advantages in the ultimate vulcanizate properties. This experiment was conducted on the two commercial SBR 1502 polymers by initially incorporating the ingredients (less the curatives) in a Banbury mixer (#2 speed, water on full) according to Table VIII.

Portions of the two masterbatches were milled for 15 minutes on a hot mill at 340° F. The resulting hot milled stocks from

Table VI. Effects of Flocculation Method on the Stability of "Hot" SBR

Polymer	SBR-1000			SBR-1007		
Flocculation method	Salt-Acid			Acid-Glue		
Hot milling treatment, 15 min.	None	300° F.	350° F.	None	300° F.	350° F.
Mooney viscosity	43	24	42	48	36	37
Points change, 1 week	+2	+ 7	+ 6	+1	+ 4	+ 2
Points change, 4 weeks	+2	+18	+20	+2	+ 6	+ 4
% Gel in benzene	Nil	36	32	Nil	Nil	Nil
Swelling index	...	46	43	...	...	...

Table VII. Effect of Flocculation Method on Polymer Stability as Reflected in the Physical Properties of Vulcanizates

Polymer	SBR-1000			SBR-1007		
Flocculation method	Salt-Acid			Acid-Glue		
Hot milling treatment	None	300° F.	350° F.	None	300° F.	350° F.
Unaged Physical Properties, 60 Minutes at 45 P.S.I.G.						
300% modulus, p.s.i.	1070	1670	1330	930	890	930
Tensile, p.s.i.	3100	2270	2070	2960	2890	2750
Elongation, %	590	380	420	620	620	600
Cut growth (0.001 in./Kc.)	0.9	5.1	3.6	0.9	1.0	1.1

Table VIII. Recipe for Cold SBR Masterbatch

	MB#1	MB#2	Time, min.
SBR 1502 (higher alkylated aryl phosphite stabilizer)	100.0		0
SBR 1502 (styrenated phenol stabilizer)		100.0	0
XX268 zinc oxide	3.0	3.0	0.5
HAF black (Philblack 0)	30.0	30.0	0.5
ISAF black (Philblack I)	25.0	25.0	2
Stearic acid	1.0	1.0	2
Paraflux	5.0	5.0	2
	164.0	164.0	4 dump

MB#1 and MB#2 were designated MB#1A and MB#2A, respectively. The stocks were then mixed with curatives on a 120° F. mill in accordance with the recipes shown in Table IX.

The stocks were cured at 45 and 90 minutes at 292° F. The physical properties of the resulting vulcanizates are given in Table X.

The advantages of the presence of an effective stabilizer during the milling of the polymer in the presence of carbon black shows up in the superior properties of vulcanizate B over vulcanizate D.

MECHANISM OF THE "SALT EFFECT"

The adverse effect of sodium chloride upon the heat stability of SBR polymer presents an interesting phenomenon. Among the suggestions that have been offered to explain it is that salt may cause physical breakdown of the stabilizer emulsion and thereby prevent effective incorporation of the stabilizing agent in the polymer. However, Table V demonstrates that the salt effect occurs in the absence of stabilizers.

Another explanation considers that the improved stability of acid-glue flocculated polymer is due to traces of retained sulfuric acid. Certain acidic substances such as acid esters of phosphoric acid markedly stabilize an SBR polymer (*7*). The effect of salt in salt-acid flocculation is visualized as involving the removal of residual sulfuric acid by interaction with traces of salt in the drying oven to produce volatile hydrogen chloride.

Table IX. Recipe for Cold SBR Vulcanizate

Stock	A	B	D	E
MB#1	164.0			
MB#1A		164.0		
MB#2			164.0	
MB#2A				164.0
Mercaptobenzothiazole	0.6	0.6	0.6	0.6
Diphenylguanidine	0.25	0.25	0.25	0.25
Sulfur	2.0	2.0	2.0	2.0

Table X. Effect of Hot Milling of Polymer on Vulcanizate Properties; Influence of Stabilizers

Stock	A	B	C	D
Stabilizer	AAP[a]	AAP[a]	SP[b]	SP[b]
Hot milling, time, min.	0	15	0	15
Tensile, p.s.i.				
45 min. cure	3150	3020	2960	2100
90 min. cure	2560	2530	2470	2080
Elongation, %				
45 min. cure	350	350	330	290
90 min. cure	260	260	260	200
Cut growth (0.001 in./Kc.)				
45 min. cure	1.67	1.73	1.80	2.17
90 min. cure	2.53	2.40	2.20	3.14
Average	2.10	2.07	2.00	2.70

[a] Higher alkylated aryl phosphite.
[b] Styrenated phenol.

Reynolds (*14*) offered a more reasonable explanation. He points out that ferric chloride is among the salts of iron which have enhanced solubility in organic media. Chloride ion in salt-acid flocculation is visualized as solubilizing trace iron in the polymer and creating an effective oxidation catalyst.

$$\begin{tikzcd} \text{Sodium chloride} \arrow[r] & Cl \arrow[dr] & \\ & & FeCl_3 \\ & \text{Iron} \arrow[ur] & \end{tikzcd}$$

Oxidation catalyst
(Soluble in polymer)

This explanation is supported by experiments which have shown that other chloride salts including calcium, magnesium, and potassium chlorides as cofflocculants in place of sodium chloride also produce poorly stabilized polymers, whereas sulfate salts such as magnesium, sodium, and potassium sulfates give more stable polymers. The samples in the top line of Figure 2 were definitely resinified, while those in the bottom line showed no resinification.

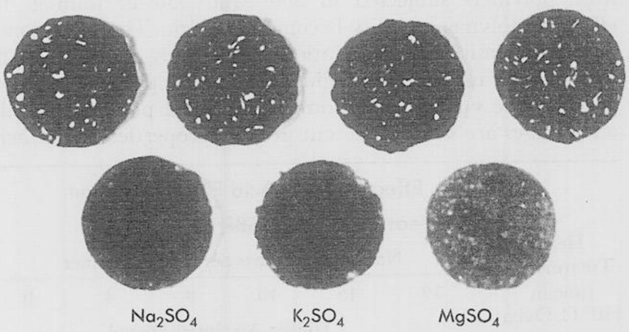


Figure 2. Effects of several salts as co-flocculants of SBR 1502
(After 90 minutes in 130° C. oven)

COLOR STABILIZATION DURING DRYING OF SBR

The emphasis on light color in nonstaining types of SBR requires the incorporation of an efficient nondiscoloring stabilizer. The heat of the drying oven may promote yellowing of the polymer, particularly at higher drying temperatures. Laboratory comparisons of several commercial stabilizers of the nonstaining type show considerable variation between the materials in their ability to prevent color development in the drying oven.

Table XI. Effect of Drying Temperature on SBR 1502

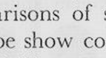
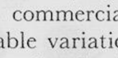
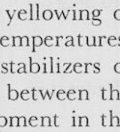
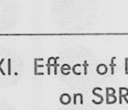
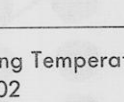
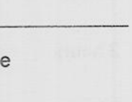
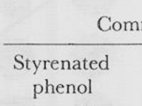
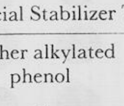
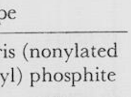
Drying Conditions,		Commercial Stabilizer Type		
Hours	° C.	Styrenated phenol	Higher alkylated phenol	Tris (nonylated aryl) phosphite
2 1/2	110			
8	85			
16	60			
16	40			

Table XII. Physical Properties of SBR 1502 Vulcanizates

(Unaged)

	300% Modulus, P.S.I.			Tensile, P.S.I.			Elongation, %		
Cure time, min. at 292° F.	25	50	100	25	50	100	25	50	100
No stabilizer	390	710	1110	2250	3570	3670	900	720	570
Tris (nonylated aryl) phosphite	400	740	1140	2500	3660	3950	950	750	600

Commercial SBR-1502 latex was treated with emulsions of three commercial nonstaining stabilizers (1.25% on the polymer) and flocculated with salt and acid. The washed crumb in each case was split into several portions and dried at several temperatures for varying periods of time. The conditions employed and the appearance of the dried crumb are illustrated in Table XI. The samples which appear darker showed varying degrees of yellowing, the color deepening with increasing drying temperature. Relatively mild drying conditions were necessary to prevent yellowing of the styrenated phenol stabilizer. The higher alkylated phenol was considerably more effective in retarding color under these conditions, while the tris (nonylated aryl) phosphite was exceptionally effective in preventing heat discoloration.

BENEFITS OF STABILIZERS ON AGING OF VULCANIZATES

Effective stabilizers for SBR polymer generally confer improved aging resistance on SBR vulcanizates. This is illustrated in experiments with tris (nonylated aryl) phosphite.

Commercial SBR-1502 latex was obtained after the shortstopping and stripping operations but prior to the incorporation of the usual stabilizer. The latex was divided, and one half was treated with an emulsion of tris (nonylated aryl) phosphite (1.25 parts per 100 of polymer) and flocculated, using the salt-acid technique. The other half was flocculated without stabilizer. The washed and dried polymers were compounded in a conventional SBR test recipe (SBR 1502, 100 parts; Wyex black, 40; Protox 166, 5; sulfur, 2; MBTS, 2) and cured at 292° F.

The tensile properties of the unaged vulcanizates as shown in Table XII do not show significant differences.

The vulcanizates were subjected to aging for five and seven days in an oxygen bomb (80° C.) and for 70 hours in the 212° F. circulating air oven. Results of the aging tests on the 50 minute cure (optimum) are shown in Table XIII. The percentage retained tensile and elongation are calculated on the basis of the unaged = 100. The protecting effect of the stabilizer on the aged vulcanizate is apparent.

Table XIII. Effect of Stabilizer on Aging of Vulcanizates

	No Stabilizer	Tris (Nonylated Aryl) Phosphite
Aged 5 days in 0_2 at 80° C.		
% tensile retained	25	50
% elongation retained	38	64
Aged 7 days in 0_2 at 80° C.		
% tensile retained	0	34
% elongation retained	0	55
Aged 70 hours at 212° F.		
% tensile retained	54	78
% elongation retained	32	47

CONCLUSIONS

The widely used method of coagulating SBR polymer by salt and sulfuric acid does not afford the level of polymer stability attainable by alternative coagulation procedures. The effects of inadequate stability in the raw polymer are reflected in lower quality of vulcanizates prepared from polymer subjected to hot processing. The importance of good polymer stability in SBR technology deserves wider consideration.

ACKNOWLEDGMENT

The authors are grateful to C. A. Carlton and Ira Williams of J. M. Huber Corp. for permission to reproduce the data showing the effects of hot Banbury mastication on SBR properties and to R. J. Reynolds for suggestions concerning the mechanism of the "salt effect" on SBR. Thanks are due W. F. Tuley, T. H. Newby, and W. A. Fairclough for encouragement and advice.

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RECEIVED for review September 23, 1958. Accepted March 18, 1959.