Preparation of Active Calcium Carbonate for Reinforcing SBR

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The purpose of the present paper is to describe the preparation of new active calcium carbonates for reinforcing SBR (styrene-butadiene rubber), together with the results of tensile tests on the vulcanizates loaded with the carbonates.

The active calcium carbonates were prepared by introducing carbon dioxide gas into aqueous calcium hydroxide containing active agents. The agents used here have two functional groups; one is reactive to calcium while the other to rubber molecule or to vulcanizer.

The SBR vulcanizates loaded with the active calcium carbonates had extremely high tensile strengths and moduli, although no significant difference in particle size was observed between active carbonates and conventional one. Sorbic acid was the most efficient of all activators, the tensile strength at break and the 300% modulus having reached as high as 167 kg./cm^2., and 40 kg/cm^2., respectively. On the other hand, those of the vulcanizate loaded with the conventional carbonate indicated only 79 kg./cm^2. and 24 kg./cm^2., respectively.

INTRODUCTION

Although silica and precipitated calcium carbonate have been widely known as typical white fillers for SBR (styrene-butadiene rubber), both of them admittedly carry some disadvantages that limit their practical application. Silica is not suitable for natural rubber because of its somewhat poor processability and of high cost. On the other hand, calcium carbonate is useful for natural rubber but not for SBR[1].

The present study is aimed at preparing calcium carbonate active for SBR. A simple procedure is chosen that calcium carbonate and some active agents are simultaneously precipitated by introduction of carbon dioxide gas into aqueous calcium hydroxide in the presence of activator.

The active agents used in this study have two functional groups; one is reactive to calcium carbonate while the other to rubber molecule or to vulcanizer. They include the following four different types:

(1) Thioglycolic acid adduct of SBR, which is obtained by the reaction of thioglycolic acid with SBR in a latex form. Active calcium carbonate is prepared by introducing carbon dioxide into the calcium hydroxide solution in the presence of the thioglycolic acid adduct of SBR latex. Thioglycolic acid is thought to act

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as a linking agent between rubber and filler, since SH and carboxylate groups are reactive toward SBR and calcium ion, respectively.

(2) Bifunctional organic compounds soluble in water, for instance, amino- or hydroxy-carboxylic acids are expected to effect jointing rubber molecule, because amine is often useful accelerator for vulcanization and hydroxyl group has an affinity to SBR probably due to its bonding ability to phenyl group of SBR through π-type hydrogen bonding[2].

(3) Calcium carbonate modified by blocking with calcium sulfide easily produced by adding sodium mono- or poly-sulfide, hydrogen sulfide or molecular sulfur into an aqueous solution of calcium hydroxide followed by heat treatment, if necessary. It contains sulfide of controlled amount and the latter may function to joint SBR in the vulcanization process.

(4) Fatty acids having double bond, for instance, maleic acid, crotonic acid and sorbic acid are expected to effect jointing rubber molecule, because an agent having double bond has been used as effective vulcanizing agent for rubber *i.e.*, maleic acid, triallylcyanurate[3] and dimaleimide[4]. Active calcium carbonate having double bond is prepared by introducing carbon dioxide gas into the calcium hydroxide solution in the presence of unsaturated fatty acid.

Fig. 1 illustrates the hypothetical mechanism of reinforcing modes of the active calcium carbonates above described.

I. CALCIUM CARBONATE ACTIVATED WITH SBR-ADDUCT

I-1. Preparation of SBR Adduct with Thioglycolic Acid

30 ml. of aqueous solution containing 3 g. of thioglycolic acid is poured under sufficient stirring into 30 g. of SBR latex (JSR ♯2108) diluted with 30 ml. of water containing 2.5 g. of sodium laurylate. After addition of 0.02 ml. of tert-butyl hydroperoxide and 0.02 ml. of tetramethylenepentamine, the mixture is allowed to stand over night. The reactien mixture is still a latex-like emulsion and can be used for the following procedure without any further treatment.

I-2. Preparation of Active Calcium Carbonate

Into the water suspension of calcium hydroxide consisting of 100 g. of calcium oxide and 500 ml. of water, the thioglycolic acid-adduct to SBR latex prepared as above is poured dropwise at room temperature and the mixture is stirred for two hours. Ten times the stoichiometric volume of carbon dioxide is then introduced into the suspension at 10°C. under vigorous agitation, whereby finely dispersed calcium carbonate is precipitated. The active filler is prepared by separation of the precipitates followed by drying them at room temperature during three weeks.

I-3. Property of SBR-Vulcanizate Loaded with the SBR-Adduct Type Filler

Table 1 shows the standard recipe for SBR, where coumaron resin is omitted

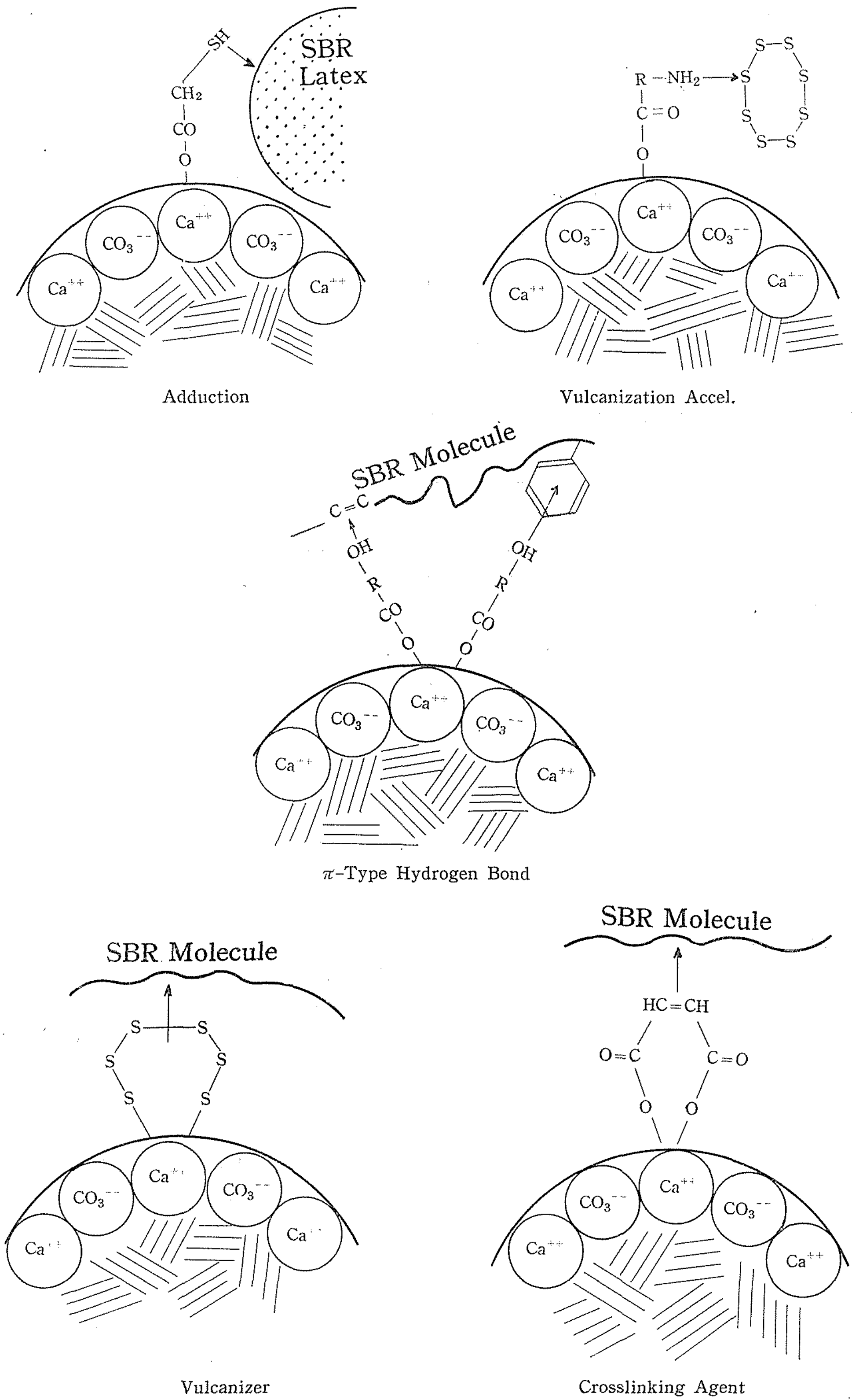


Fig. 1. Hypothetical mechanism of reinforcing modes of the active calcium carbonates.

Table 1. Standard recipe for vulcanization of SBR.

SBR[a]	100
Zinc oxide	5
Sulfur	2
Stearic acid	1
Accelerator DM[b]	1.5
Accelerator M[c]	0.5
Filler	100

[a] Polysar Krylene NS. [b] Benzothiazyl disulfide.
[c] Mercaptobenzothiazole.

in order to avoid staining. Compounding was carried out on an open roll and the curing by press at 143°C.

In Table 2, the physical properties of the vulcanizates loaded with active

Table 2. Properties of SBR vulcanizates loaded with calcium carbonate activated by SBR adduct and with conventional calcium carbonate.

Type of $CaCO_3$	Cure time (min.)	Modulus at 300% (Kg./cm.^{2})	Tensile strength at break (Kg./cm.^{2})	Elongation at break (%)	Hardness
Conventional $CaCO_3$	15	12.7	35	516	56
	25	13.7	35	514	59
	40	13.7	33	505	58
Active $CaCO_3$	15	34.5	88	586	58
	20	35.7	111	605	58
	30	35.6	98	673	58

calcium carbonate are compared to those with conventional calcium carbonate. It is noticed there that the former vulcanizates have extremely high tensile strength and modulus. In these vulcanizates, the tensile strength at break is three times higher and modulus at 300% elongation is two to three times higher than in the conventional vulcanizates.

Figs. 2(a) and 2(b) are the electronmicroscopic photographs of the conventional and active fillers, respectively. Between these photographs no significant difference can be observed in particle size or dispersion mode. The situation suggests that the activity characteristic of adduct-filler may be attributed to the chemical but not to the physical property of the filler.

II. CALCIUM CARBONATE ACTIVATED WITH AMINO ACIDS

As amino acids, sodium glutamate (1), hystidine (2), lysine (3), arginine (4), phenylalanine (5) and *p*-aminobenzoic acid (6) are examined.

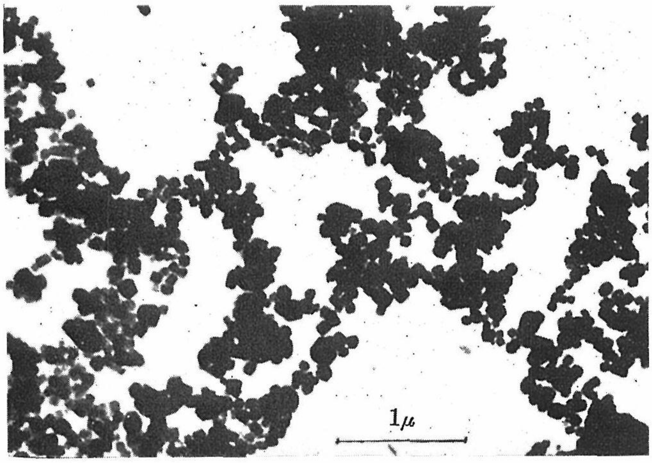


Fig. 2 (a). Electronmicroscopic photograph of conventional calcium carbonate (20,000 magnifications).

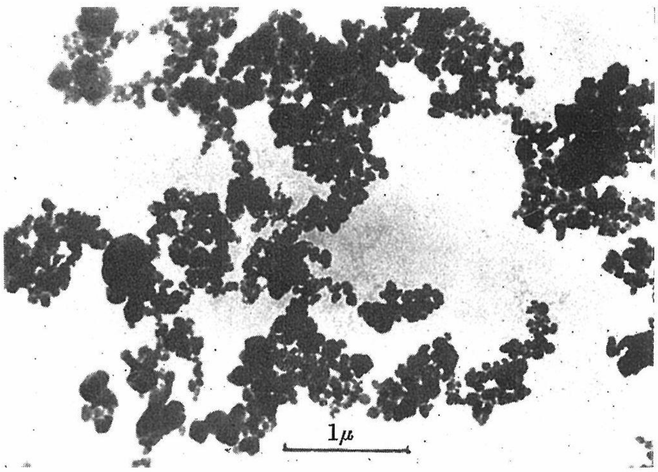
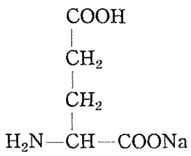
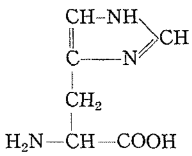


Fig. 2 (b). Electronmicroscopic photograph of active calcium carbonate containing SBR-adduct (20,000 magnifications).


(1)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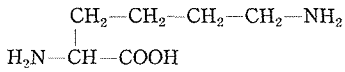
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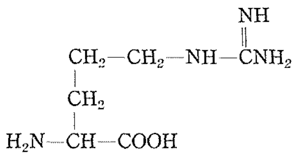
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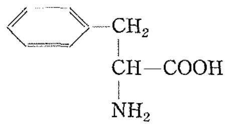
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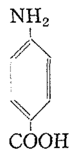

(6)

Active fillers of this type were prepared by the same procedure as described above. 2.5 g. of amino acid is added to calcium hydroxide solution containing 100 g. of calcium oxide and 2000 ml. of water and is allowed to react with carbon dioxide gas at 10°C. which is introduced the rate of 8 l. per minute. The use of these active fillers in the same recipe as shown in Table 1 resulted in the increase in tensile strength and modulus as can be seen in Table 3.

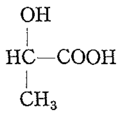
Table 3. Properties of SBR vulcanizates loaded with calcium carbonates activated by amino acids.

Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
Sodium glutamate	10	18.5	146	713	60
	15	20.7	138	688	63
	20	20.4	139	700	63
Lysine	20	16.1	129	738	60
	25	17.4	124	700	62
	35	18.5	121	688	62
Hystidine	20	8.8	83	825	54
	25	9.1	100	763	56
	35	13.1	90	700	58
Arginine	20	15.4	85	625	61
	25	13.9	62	675	61
	35	15.1	60	588	61
Phenyl-alanine	20	7.4	97	888	50
	25	10.3	90	800	56
	35	10.5	82	750	56
p-Amino-benzoic acid	20	9.4	65	825	53
	25	12.8	67	788	57
	35	15.2	60	750	59

The data listed in Table 3 indicate that all of the amino acid used act as activators for the SBR vulcanization by calcium carbonate. Sodium glutamate is the most efficient of all, *i.e.*, the tensile strength at break is four times as high as the strength attained by using the conventional calcium carbonate.

III. CALCIUM CARBONATE ACTIVATED WITH HYDROXY-CARBOXYLIC ACIDS

Lactic acid (7), *p*-hydroxybenzoic acid (8) and gallic acid (9) are examined as activator. Preparation and examination of active calcum carbonates are essentially the same as described in a preceding chapter.



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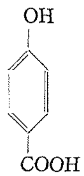

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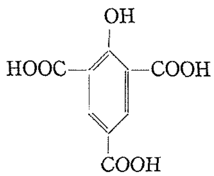


(9)

They also enhance tensile strength as seen in Table 4. Gallic acid is the most powerful activator but its practical use may be limited because of the extensive development of brown color in the vulcanization process.

Table 4. Properties of SBR vulcanizates loaded with calcium carbonates activated by hydroxycarboxylic acids.

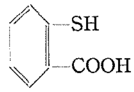
Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
Lactic acid	20	8.2	87	900	57
	25	10.9	54	788	60
	35	13.0	63	688	60
p-Hydroxybenzoic acid	20	11.3	88	888	54
	25	13.4	69	700	58
	35	15.2	63	688	60
Gallic acid	20	8.6	110	875	52
	25	12.5	105	850	56
	35	14.8	100	800	57

IV. CALCIUM CARBONATE ACTIVATED WITH THIOGLYCOLIC ACID

Thioglycolic (10) and thiosalicylic acids (11) were tested. They also exhibited reinforcing action though it was somewhat in low degree. The low activity of thioglycolic acid may be due to deactivation in the course of drying because they are vulnerable to oxidation.

$HS-CH_2-COOH$

(10)



(11)

Table 5. Properties of SBR vulcanizates loaded with calcium carbonates activated by thiol acids.

Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
Thioglycolic acid	20	5.3	75	1095	50
	25	9.5	85	850	52
	35	12.6	64	750	54
Thiosalicilic acid	20	7.3	45	850	56
	25	7.2	50	800	55
	35	8.8	50	750	57

In order to avoid the oxidation it is necessary to protect the thiol group by other reagents prior to precipition. The use of calcium carbonate modified with SBR-adduct is much more advantageous in this respect.

V. CALCIUM CARBONATE ACTIVATED WITH CALCIUM SULFIDE

Calcium carbonate was prepared from calcium hydroxide in the presence of calcium sulfide, whereby the simultaneous precipitation of calcium carbonate and calcium sulfide occurs to give a highly active filler for SBR. The activity of the filler may be due to the active sulfide groups located on the surface of particle, which will react with rubber molecule in the vulcanization process.

The following methods were adopted to prepare the active filler: A suspension of 12.5 g. of calcium oxide and 25 g. of sulfur in 350 ml. of water was boiled for one hour to turn calcium sulfide suspension. 42 ml. of sulfide suspension (equivalent to 3 g. of free sulfur) was added to milk of lime consisting of 100 g. of calcium oxide and 200 ml. of water. A stream of gaseous carbon dioxide was then passed through the suspension mixture for about an hour at the rate of 8 l. per minute at 10°C. The resulting precipitate (active filler) was collected and dried at room temperature for about three weeks. Direct reaction of sulfur with calcium hydroxide suspension was also possible by heating the mixture of free sulfur and milk of lime. For example, 100 g. of calcium oxide and 3 g. of sulfur were put into 2 l. of water, followed by boiling for about an hour. Into the suspension mixture carbon dioxide was introduced in the same way as above.

Table 6 indicates the excellent property of SBR-vulcanizates compounded with active calcium carbonate, where extremely high values may be seen in ten-

Table 6. Properties of SBR vulcanizates loaded with calcium carbonates activated by sulfide.

Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
Calcium sulfide	10	18.7	157	625	57
	15	19.5	138	600	59
	20	19.2	133	600	60
Sulfur	10	18.1	157	638	56
	15	20.1	152	613	58
	20	19.1	143	600	58

sile strength, *i.e.*, 150 kg./cm.^{2} or more at 600% elongation at break.

VI. DETAILED PROPERTY OF FILLER ACTIVATED WITH SODIUM GLUTAMATE

In order to elucidate the chemical behavior of activated calcium carbonate in vulcanization, a series of experiments were undertaken using a varying amount of sodium glutamate as activator in special comparison with the case, in which sodium glutamate was mechanically added to SBR. Table 7 gives the data in the latter case, where the activity of sodium glutamate can hardly be recognized.

Table 7. Effect of sodium glutamate on vulcanization of SBR. (Glutamic acid was added directly to SBR.)

Amount of Na-glutamate (PHR)[a]	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
0	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
1	20	14.2	70	713	64
	25	14.8	55	650	65
	35	15.2	58	650	67
2	20	12.4	60	775	58
	25	15.2	64	675	64
	35	15.9	63	675	65

[a] PHR : Grams per hundred grams of rubber.

On the other hand, the vulcanizates are reinforced appreciably when they are loaded with calcium carbonate activated by the glutamate, as shown in Table 8. The modulus at 300% elongation increases in rough proportion to the amount of the glutamate used, while the tensile strength at break tends to reach its flat maximum at the glutamate concentration around 2%.

Table 8. Effect of sodium glutamate on vulcanization of SBR. (Sodium glutamate was added to aqueous solution of calcium hydroxide to obtain the active calcium carbonate.)

Amount of Na-glutamate[a]	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
0	20	16.2	32	568	64
	25	16.4	32	550	69
	35	16.5	26	488	68
1	15	13.5	133	725	57
	20	13.8	132	738	57
	25	14.7	124	675	60
2	10	18.5	146	713	60
	15	20.7	138	688	63
	20	20.4	139	700	63
3	10	21.3	131	713	61
	15	24.0	130	675	62
	20	23.5	129	663	63
4	10	24.1	144	750	65
	15	26.7	132	700	65
	20	26.3	148	700	64
5	10	24.5	96	700	68
	15	24.2	101	700	68
	20	28.2	92	675	67

[a] Grams per hundred grams of calcium oxide.

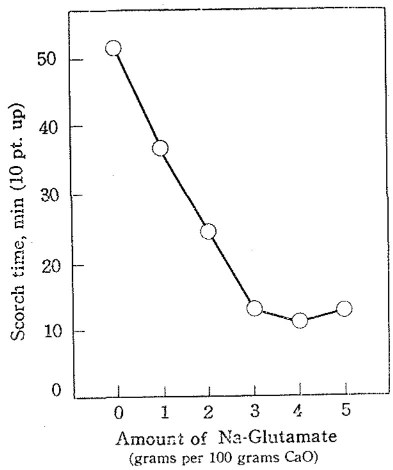


Fig. 3. Scorch time vs amounts of Na-glutamate.

The effect of sodium glutamate on curing was examined by measuring the scorch time at 121°C. with the use of the Mooney viscometer. Fig. 3, in which the scorch time of SBR loaded with the active calcium carbonate is plotted against the amount of sodium glutamate used, demonstrates clearly the acceleration effect of active filler on vulcanization. No such effect was observed when the glutamate was added directly to SBR loaded with conventional calcium carbonate of the same amount.

These characteristic effects of the active calcium carbonate suggests the ocurrence of chemical bonning of glutamic acid to calcium carbonate.

The contents of sodium glutamate in the active calcium carbonate were determined by the following method:

Five parts of calcium hydroxide solution composed of 100 g. of calcium oxide and 2000 ml. of water prepared, four of which were charged separately with 1, 2, 3 and 4 g. of the glutamate, the last one part having been used for blank test. Carbon dioxide gas was then introduced into every part of the solution and the resulting precipitates of calcium carbonate were filtered off and washed three times with 1000 ml. of water. Each filtrate was mixed with its washings and, utilizing the ninhydrine reaction of glutamates the mixture were subjected to photoelectric colorimetry of the sodium glutamate remaining unchanged. The results are showh in Table 9. As can be seen in Table 9 major part of the glutamate added to calcium hydroxide has been chemically bound to calcium carbonate.

Table 9. Contents of Na-glutamate in active calcium carbonate.

Amounts of Na-glutamate used (g./100 g. CaO)	Observed amounts of Na-glutamate in filtrate and washings (g.)	Extent of reaction (%)	Contents of Na-glutamate combined with $CaCO_3$ (g./1 g. $CaCO_3$)
1.0	0.10	90	0.05
2.0	0.40	80	0.09
3.0	0.51	83	0.14
4.0	0.71	82	0.18

It was also found that sodium glutamate is a useful dispersing agent for calcium carbonate. Figs. 4 to 9 are the electromicroscopic photographs of calcium carbonates, which show that particle size becomes smaller with increasing amount of the glutamate used. For instance, the average diameter of active filler particles including 2% glutamate is about 0.03μ, while that of the conventional filler particles without glutamate is 0.08 μ. Figs. 10 and 11 are the photographs of vulcanized rubbers loaded with the active and conventional fillers, respectively. Highly fine dispersion is observed in the case of the active filler. Sodium glutamate is thus seen to improve the dispersion of filler into rubber matrix.

VII. CALCIUM CARBONATE ACTIVATED WITH UNSATURATED FATTY ACID

VII-1. Activators

As unsaturated fatty acid; maleic acid (12), maleic anhydride (13), acrylic acid (14), crotonic acid (15), vinyl acetic acid (16), methacrylic acid (17) and sorbic acid (18) are examined.

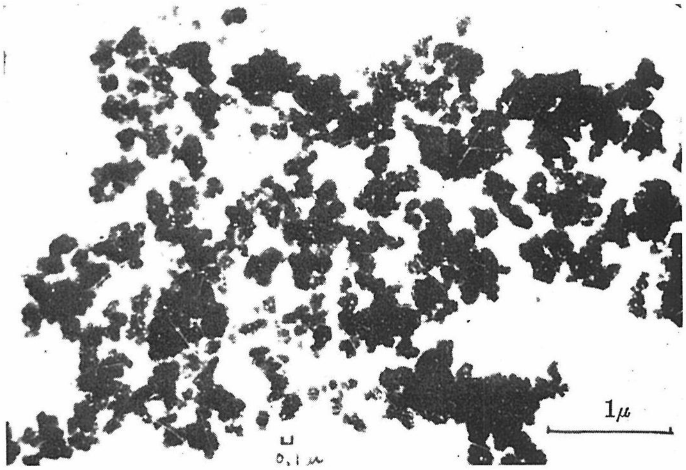


Fig. 4. Electronmicroscopic photograph of conventional calcium carbonate (20,000 magnifications).

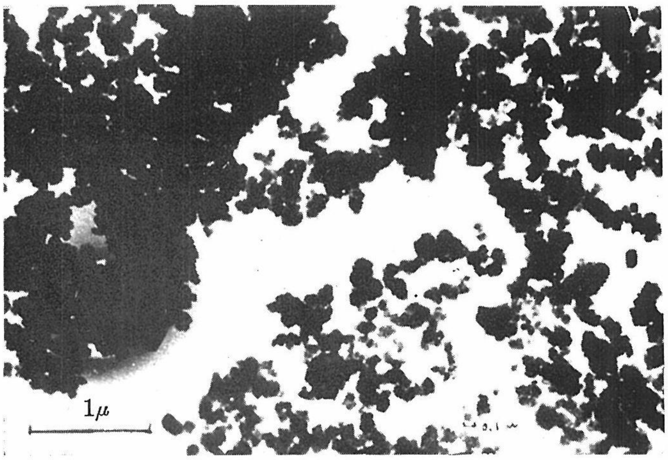


Fig. 5. Electronmicroscopic photograph of active calcium carbonate (activator: 1 g. of sodiumglutamate per 100 g. of calcium carbonate; 20,000 magnifications).

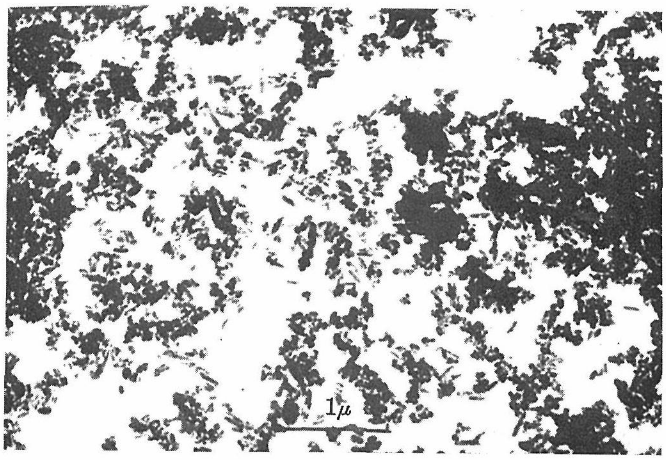


Fig. 6. Electronmicroscopic photograph of active calcium carbonate (activator: 2 g. of sodium glutamate per 100 g. of calcium oxide; 20,000 magnifications).

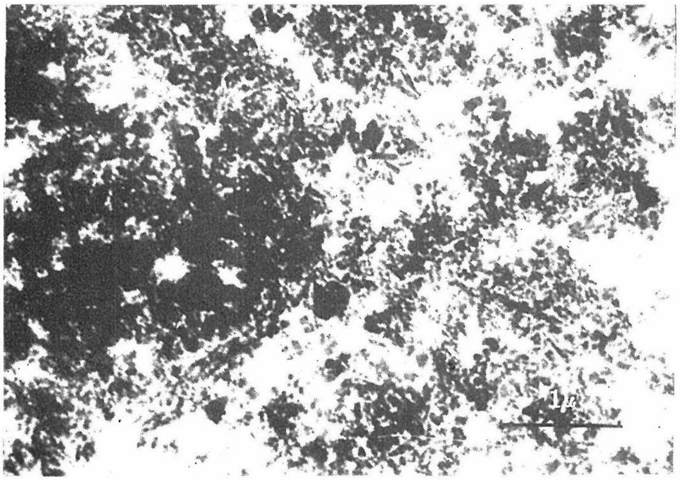


Fig. 7. Electronmicroscopic photograph of active calcium carbonate (activator : 3 g. of sodiumglutamate per 100 g. of calcium oxide ; 20,000 magnifications).

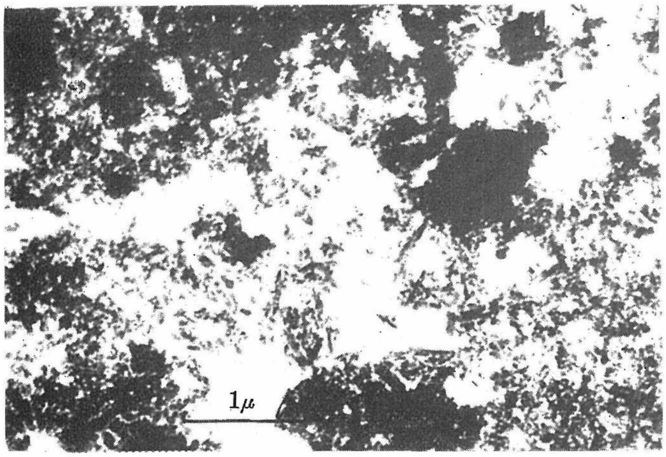


Fig. 8. Electronmicroscopic photograph of active calcium carbonate (activator : 4 g. of sodiumglutamate per 100 g. of calcium oxide ; 20,000 magnifications).

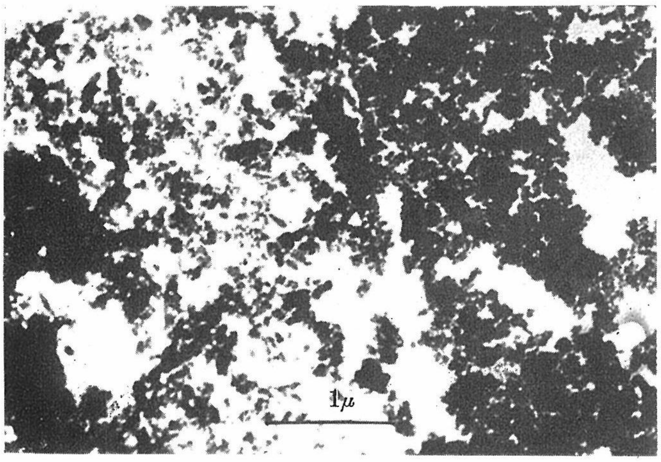


Fig. 9. Electronmicroscopic photograph of active calcium carbonate (activator : 5 g. of sodiumglutamate per 100 g. of calcium oxide ; 20,000 magnifications).

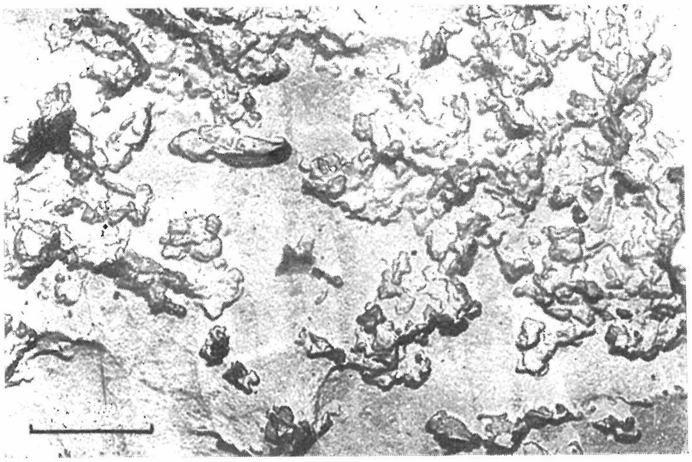


Fig. 10. Electronmicroscopic photograph of oonventional calcium carbonate in SBR vulcanizates ; 20,000 magnifications).

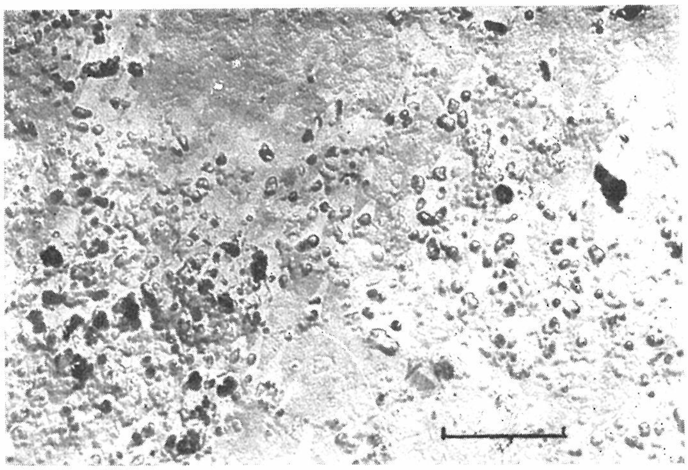
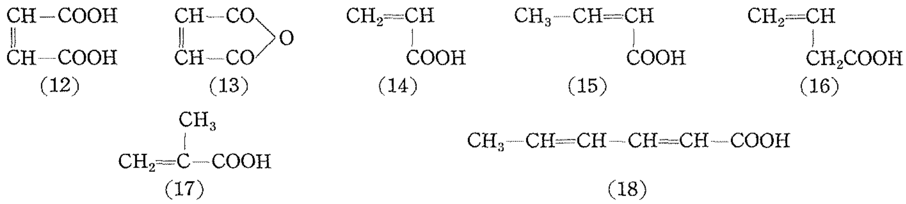


Fig. 11. Electronmicroscopic photograph of active calcium carbonate in SBR vulcanizates (activator : 2 g. of sodium glutamate per 100 g. of calcium oxide ; 20,000 magnifications).



(12) (13) (14) (15) (16) (17) (18)

VII-2. Preparation of Active Calcium Carbonate

The preparation of active filler of this type is as follows:

0.052 moles of the activator are added to calcium hydroxide solution containing 100 g. of calcium oxide and 2 l. of water and the solution is reacted with carbon dioxide gas diluted 4-fold with air at 10°C. until the solution indicates no longer alkali to phenolphthalein. The precipitated calcium carbonate is allowed to dry in the air at 50±5°C. until the water contents below 1%, followed by grinding a crusher.

VII-3. Properties of SBR Vulcanizate Loaded with Calcum Carbonate Activated with Unsaturated Fatty Acid

Samples were prepared by compounding according to the recipe given in Table 1 and by curing at 141°C. In Table 10 the physical properties of the vulcanizate loaded with the calcium carbonate activated with maleic acid are compared to those with conventional calcium carbonate and the comparison between maleic acid and succinic acid is indicated to elucidate an effectiveness of double bond in activator at the same time. It is noticed that the vulcanizate loaded with the carbonate activated with maleic acid have extremely higher tensile strength and modulus.

Table 10. Properties of SBR vulcanizates loaded with calcium carbonates activated with aliphatic di-carboxylic acids*).

Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	23.8	72	690	54
	30	23.9	79	680	56
	40	24.5	79	660	56
Succinic acid	30	23.1	87	710	54
	40	24.9	96	680	57
	50	25.3	92	660	57
Maleic acid	15	31.9	113	680	62
	20	32.6	122	700	63
	30	34.1	122	700	63

*) 0.051 moles (ca. 6 g.) of acid per 100 g. of calcium oxides.

Figures 12(a), (b) and (c) are the electromicroscopic photographs of the above three sorts of calcium carbonate.

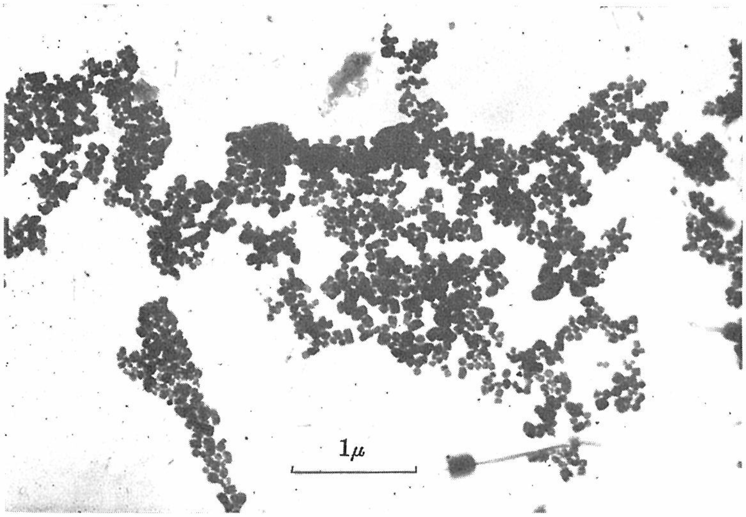


Fig. 12 (a). Electronmicroscopic photograph of conventional calcium carbonate (20,000 magnificotions).

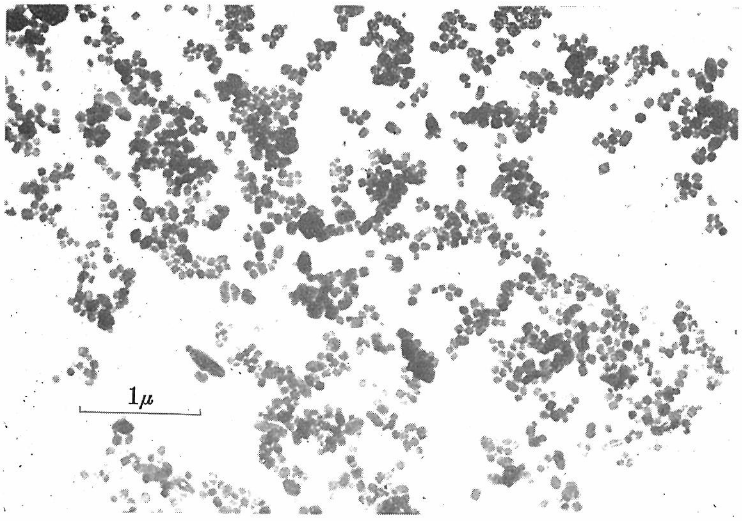


Fig. 12 (b). Electronmicroscopic photogroph of calcium carbonate activated with succinic acid (20,000 magnifications).

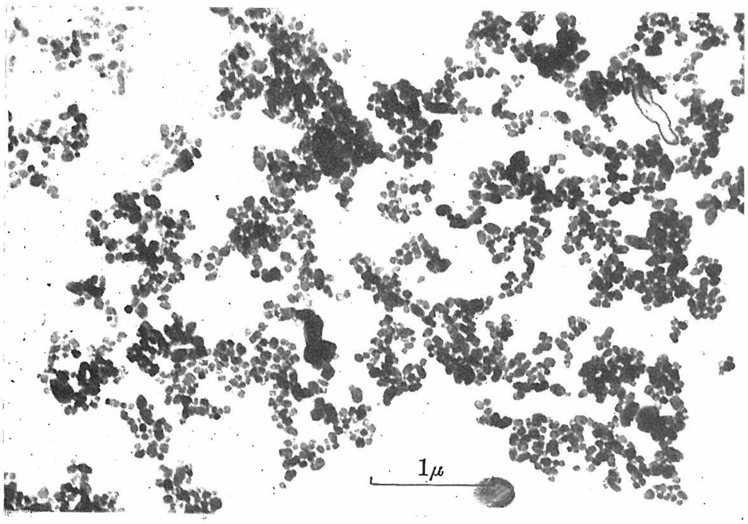


Fig. 12 (c). Electronmicroscopic photograph of calcium carbonate activated with maleic acid (20,000 magnifications).

Among these photographs no significant difference can be observed in particle size or dispersion mode. The situation suggests that the activity characteristic of the filler activated with maleic acid may be attributed to the effect of double bond but not to the physical property of the filler.

Table 11. Properties of SBR vulcanizates loaded with calcium carbonates activated with unsaturated aliphatic carboxylic acids*).

Activator	Cure time (min.)	Modulus at 300% (kg./cm.^{2})	Tensile strength at break (kg./cm.^{2})	Elongation at break (%)	Hardness
None	20	23.8	72	690	54
	30	23.9	79	680	56
	40	24.5	79	660	56
Maleic acid	15	31.9	113	680	62
	20	32.6	122	700	63
	30	34.1	122	700	63
Maleic anhydride	15	28.0	115	730	60
	20	28.4	126	710	60
	30	29.4	112	700	60
Acrylic acid	30	18.0	89	800	51
	40	20.1	93	750	53
	50	21.2	102	730	54
Crotonic acid	15	26.3	152	640	59
	20	34.0	145	640	59
	30	34.1	144	630	59
Vinyl acetic acid	30	20.5	97	730	52
	40	21.9	98	720	54
	50	22.9	116	670	56
Methacrylic acid	30	21.2	107	770	52
	40	22.1	108	730	54
	50	24.5	123	720	56
Sorbic acid	15	40.1	163	670	61
	20	40.4	167	670	62
	30	38.4	152	660	62

*) 0.051 moles of acid per 100 g. of calcium oxide.

The data listed in Table 11 indicate that all of the unsaturated fatty acids are more or less useful activators for calcium carbonate. The vulcanizate loaded with the carbonate activated with sorbic acid is the most efficient of all, *e.g.*, the tensile strength at break and 300% modulus indicate 167 kg./cm.^{2} and 40 kg./cm.^{2}, respectively. On the other hand, those of the vulcanizate loaded with the conventional carbonate indicate only 79 kg./cm.^{2} and 24 kg./cm.^{2}, respectively.

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