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Preparation of Reinforcing Fillers from Japanese Acid Clays with Lime and by Calcination. II. Optimum Conditions for the Preparation of Good Hard Clays and Evaluation of Their Reinforcing Properties

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In order to find the optimum conditions for the preparation of good reinforcing filler from Matsune (**M**) and Nakajo (**N**) acid clays with lime and by calcination, investigations were carried out by changing the amount of alkali (1.25—60% CaO), the temperature of thermal treatment (110—800 °C) and the subsequent mechanical disintegration time (6—24 hr). The required conditions were found to be: amount of alkali, 3% for **M** and 6% for **N**; calcination at 600 °C for 1.5 hr; disintegration time around 18 hr. The deviation in the optimum amount of alkali was attributed to the difference of mineralogical constituents. The products pulverized gave the SBR-1502 compounds good reinforcing properties comparable to those of Dixie Clay. Investigation was also carried out on the influence of manual and mechanical mixing of the raw materials, the mode of disintegrating the calcined matter by either wet ball-milling or dry pulverization, and the effect of sieving the pulverized product in wet or dry state on the reinforcing properties of the prepared fillers. A variable loading test with hard clay **M** up to 150 PHR proved that its reinforcing properties are comparable to those of the reference filler. The maximum reinforcement for the elastomer was found to be about 50 PHR for hard clay **M** and about 100 PHR for the reference filler.

The availability of some Japanese acid clays as raw material for the preparation of a reinforcing filler of elastomers was reported previously.1) Acid clays such as **M** and **N** containing normal and/or abnormal montmorillonite and α-cristobalite as principal constituents were found to be suitable. However, no reinforcing filler could be prepared from Kuramitsu (**K**) acid clay containing halloysite as a major component in the randomly mixed layers of kaolinite and montmorillonite with no excess silica. **M** provided less colored and much better reinforcing fillers than **N**.

Treatment with hydrated lime (10% CaO) followed by calcination (600 °C, 1.5 hr) causes irreversible contraction in the montmorillonite minerals as well as the formation of calcium silicates covering the surfaces of montmorillonite crystallites. This gives rise to favorable changes in the inherent properties such as adsorptivity, pH, swelling, bulk density and specific gravity. The products pulverized exhibit considerable reinforcing effects on SBR-1502, which exceed Silene EF in the tensile strength and elongation of the loaded compounds. However, the reinforcing character still falls short of Dixie Clay.

This paper deals with further investigations to find the optimum conditions for the preparation of a good hard clay from the acid clays, Matsune **M** and Nakajo **N**; the amount of alkali, temperature of thermal treatment and subsequent mechanical disintegration time. Effects of mixing the raw materials manually and mechanically and of sieving the pulverized product in wet and in dry state on the reinforcing properties of the prepared filler were also investigated. Variations in the reinforcing characters due to the loading amounts were examined up to 150 PHR with hard clay **M**. The reinforcing effects of the prepared fillers on SBR-1502 were evaluated in comparison with those of Dixie Clay. Excellent fillers comparable to the references were obtained from both specimens.

Experimental

Raw Materials. *Acid Clays*: The same acid clays, **M** and **N**, as in the preceding paper1) were used. Table 1 shows the chemical composition of the specimens, from which the structural formulas and excess silica were estimated.

M, white and powdery, consists only of normal montmorillonite containing excess silica (34%), whereas **N**, light yellowish gray and crushed under 6 mesh, consists of montmorillonites containing excess silica (13%), in which the amount of abnormal montmorillonite is greater than that of normal one.

Quicklime: Calcium oxide lumps (10—30 cm^3) of reagent grade were pulverized and grains smaller than 60 mesh were chosen.

Preparation of Reinforcing Fillers. The method essentially the same as before1) was followed. Treatment was modified as follows: The amounts of alkali were varied in the range 1.25—60% CaO in weight of the acid clay dehydrated at 110 °C for 4 hr; the temperature of thermal treat-

TABLE 1. CHEMICAL COMPOSITION OF ACID CLAY

Sample	Symbol	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	$H_2O(+)$	$H_2O(-)$	Total	SiO_2/Al_2O_3
Matsune acid clay	**M**	67.12	0.08	11.53	0.79	0.27	3.07	1.10	0.18	0.07	5.10	10.85	100.16	9.87
Nakajo acid clay	**N**	53.35	0.16	14.94	2.75	0.09	4.80	0.06	0.28	0.06	7.30	16.46	100.25	6.06

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1) H. Rai and J. Yamada, This Bulletin, **45**, 1540 (1972).

ment was 110—800 °C and the time of subsequent mechanical disintegration for the calcined matter 6—24 hr.

Effects of Mixing, Disintegration, and Sieving. The effect of mixing the raw materials according to the ball-milling method and that of manual grinding with a mortar and pestle was compared. The difference in mechanical disintegration in wet and dry states of the calcined matter was examined respectively by ball milling and dry pulverization with an atomizer (Tokyo Atomizer Co., Ltd). The effect of sieving the pulverized product in dry and wet states was also investigated.

Compounding Test. The same compounding test as described before1) was carried out to screen the reinforcing fillers prepared. The effect of loading amounts of the best hard clay on the reinforcement of SBR-1502 was examined up to 150 PHR in comparison with those of Dixie Clay.

Results and Discussion

The Optimum Conditions for The Preparation of A Good Reinforcing Filler. *A. Preparation and Reinforcing Properties of Hard Clay N*: The amounts of alkali were made to be 3, 6, 10, 30, 50, or 60% CaO in weight. The raw materials were mechanically mixed in wet state with a porcelain ball mill for 1 hr. In view of the structural changes in acid clay revealed on the DTA and TGA thermograms,1) the mixture dried at 110 °C was calcined at 400 °C to attain complete dehydration, at 600 °C for mid-dehydroxylation and

TABLE 2. REINFORCING EFFECTS OF THE FILLERS DERIVED FROM **N** ON SBR-1502 IN COMPARISON WITH THOSE OF DIXIE CLAY

Sample No.	Lime CaO (%)	Calcination		Vulcanization time, min	Tensile strength kg/cm^2	300% Modulus kg/cm^2	Elongation %	Hardness JIS
		Temperature, °C	Time, hr					
1	10	800	1	8	18.3	12.5	474	56
				12	22.0	13.1	445	56
				16	26.0	12.8	517	55
2	30	800	1	8	28.3	17.3	420	60
				12	24.3	16.5	397	59
				16	24.3	16.6	304	61
3	50	800	1	8	24.3	18.6	346	64
				12	21.9	19.5	294	64
				16	24.3	19.1	323	64
4	10	600	1	8	74.0	17.3	851	53
				12	71.9	17.2	832	53
				16	76.1	17.8	846	54
5	30	600	1	8	53.3	27.2	538	64
				12	47.6	26.3	492	62
				16	47.0	26.2	486	63
6	50	600	1	8	33.3	23.8	401	65
				12	31.7	24.0	361	64
				16	33.3	23.8	375	66
7	10	400	1.5	8	51.8	12.8	891	45
				12	53.3	14.0	827	51
				16	57.8	14.2	827	52
8	30	400	1.5	8	64.0	22.1	620	51
				12	56.4	21.0	617	56
				16	52.7	20.5	618	55
9	60	400	1.5	8	32.6	25.9	320	60
				12	31.0	27.2	317	62
				16	28.2	25.3	299	62
10	3	400	1.5	8	22.7	8.0	888	40
				12	31.4	10.2	920	46
				16	33.3	11.1	834	49
11	3	600	1.5	8	51.8	14.5	804	39
				12	70.1	16.5	942	48
				16	74.9	18.4	882	51
12	3	800	1.5	8	32.6	14.2	541	51
				12	30.2	14.7	521	52
				16	27.5	14.6	509	53
13	6	600	1.5	8	68.4	13.3	925	42
				12	85.7	14.2	879	49
				16	93.8	16.2	831	51
14	Dixie Clay, reference filler			8	94.5	23.6	787	53
				12	94.1	27.1	785	55
				16	96.3	27.7	722	56

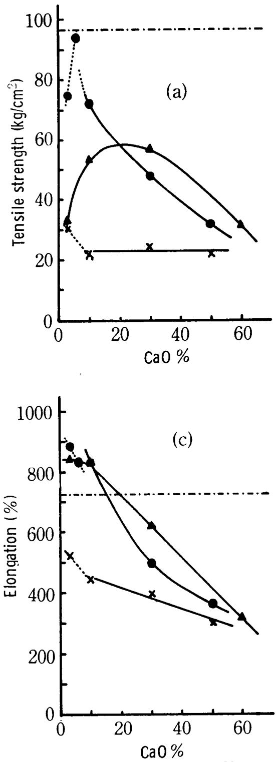

Fig. 1. Changes with lime (CaO 3—60%) and calcination (400—800 °C, 1—1.5 hr) in the reinforcing effects of **N** hard clay on SBR-1502 as compared with those of Dixie Clay.
×····× 800 °C, 1.5 hr: ●····● 600 °C, 1.5 hr; ▲—▲ 400 °C, 1.5hr; ×—× 800°C, 1hr; ●—● 600°C, 1hr; -·-·-· Dixie Clay

at 800 °C for complete dehydroxylation for 1 or 1.5 hr. The product was disintegrated by wet ball-milling at room temperature for 18 hr followed by filtration and drying at 110 °C. The dried matter was pulverized with an atomizer to give a reinforcing filler. The reinforcing effects of the prepared fillers on SBR-1502 are given in Table 2. Figures 1 (a)—(d) show the results obtained under the optimum conditions.

*Tensile Strength (*kg/cm^2*)*: The fillers prepared with hydrated lime (3—50% CaO) followed by calcination at 800 °C for 1 or 1.5 hr gave the lowest tensile strength which was almost independent of the variation in alkali corresponding to only 25% value of Dixie Clay (Fig. 1-(a)). Those treated with 3—60% CaO and by subsequent calcination at 400 °C for 1.5 hr exhibited a maximum tensile strength around 20% CaO, which was equivalent to about 60% value of Dixie Clay. Those prepared with 3—50% CaO followed by calcination at 600 °C for 1 or 1.5 hr showed a noticeable increase in the tensile strength with the decrease in the amount of alkali. The specimen treated with 6% CaO and by subsequent calcination at 600 °C for 1.5 hr exhibited the highest tensile strength comparable to that of Dixie Clay. However, the one treated with 3% CaO followed by the same calcination as the former showed an abrupt decrease in tensile strength about 78% value of Dixie Clay.

Modulus (300%, kg/cm^2*)*: Fillers prepared with 3—60% CaO and by subsequent calcination at 400 °C for 1.5 hr or 800 °C for 1 hr showed increase in the moduli with the increase in the amount of alkali (Fig. 1-(b)). The filler calcined at a lower temperature showed a greater rate in the increase in modulus than the one treated at a higher temperature with the same amount of alkali. Those prepared with 3—50% CaO followed by calcination at 600 °C for 1 hr exhibit an almost maximum modulus comparable to that of Dixie Clay with 30% CaO. The fillers prepared with CaO less than 10% and by calcination at temperatures 400—800 °C for 1 or 1.5 hr showed relatively lower modulus than that of Dixie Clay. This is in remarkable contrast to the case of hard clay **M**, and might be ascribed to the difference in the amounts of excess silica and abnormal montmorillonite.

Elongation (%): The fillers treated with CaO less than 10% followed by calcination at 400 or 600 °C for 1.5 hr gave considerably higher elongation than that of Dixie Clay (Fig. 1-(c)). The elongation decreases in proportion to the amount of alkali. When specimens were prepared with equal amount of alkali, the higher the calcinating temperature, the lower the elongation. The rate of decreasing elongation due to the amount of alkali was found to be great for the fillers calcined at 400 °C, but was relatively small for those treated at 800 °C.

Hardness (JIS): The fillers calcined at 400 °C for 1.5 hr or 800 °C for 1 hr showed a linear increase in hardness with the amount of alkali (Fig. 1-(d)). Those calcined at 600 °C for 1—1.5 hr afforded greater rate of increasing hardness with the amount of alkali than the former two series. A tendency to approaching a saturated value (64) was observable at 30% CaO, which was much greater than that (56) of Dixie Clay and comparable to that (65)[1] of Silene EF.

The optimum conditions of treatment with lime and by calcination for **N** may be concluded to be around 6% CaO and 600 °C for 1.5 hr, respectively. It is

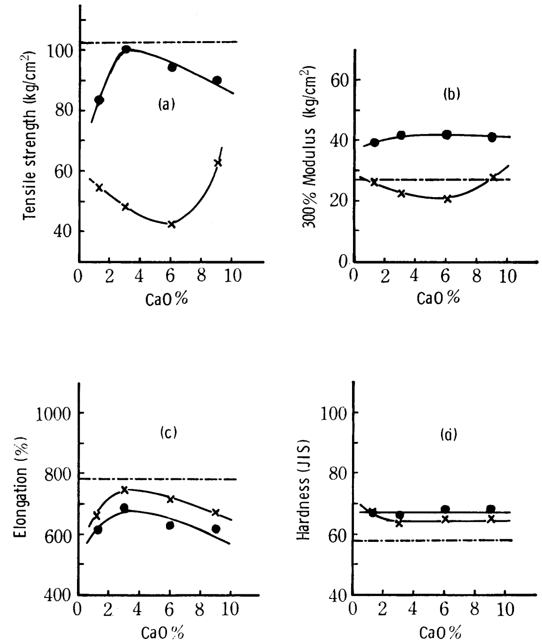

Fig. 2. Changes with lime (CaO 1.25—9%) and thermal treatment (110 °C, 5 hr; 600 °C, 1.5 hr) in the reinforcing effects of **M** hard clay on SBR-1502 as compard with those of Dixie Clay.
×—× 110°C, 5hr; ●—● 600°C, 1.5hr; -·-·-· Dixie Clay

TABLE 3. REINFORCING EFFECTS OF THE FILLERS DERIVED FROM **N** ON SBR-1502 IN COMPARISON WITH THOSE OF DIXIE CLAY

Sample No.	Lime CaO (%)	Calcination Temperature, °C	Calcination Time, hr	Vulcanization time, min	Tensile strength kg/cm²	300% Modulus kg/cm²	Elongation %	Hardness JIS
1	1.25	110	5	8	55.6	24.8	723	65
				12	53.8	26.3	660	67
				16	55.9	26.2	668	67
2	3	110	5	8	50.1	21.0	802	62
				12	48.2	22.8	750	64
				16	48.7	23.1	684	65
3	6	110	5	8	38.5	19.0	770	62
				12	40.5	20.2	700	64
				16	41.9	20.4	717	65
4	9	110	5	8	58.7	26.7	727	63
				12	61.4	27.3	674	66
				16	62.2	27.8	677	65
5	1.25	600	1.5	8	84.8	35.0	750	64
				12	82.8	39.8	610	66
				16	83.6	38.4	616	67
6	3	600	1.5	8	94.2	35.4	793	62
				12	95.8	43.2	661	66
				16	100.1	41.4	688	66
7	6	600	1.5	8	86.8	35.9	667	65
				12	93.7	42.0	627	68
				16	91.9	39.9	660	68
8	9	600	1.5	8	87.9	36.3	640	65
				12	90.2	40.3	621	68
				16	88.4	45.6	602	68
9	Dixie Clay, reference filler			8	97.1	25.1	802	56
				12	102.6	27.3	783	58
				16	90.8	27.8	715	60

noticeable that regardless of the calcinating temperature, the reinforcing properties of the prepared fillers tend to approach their respective constant values around 60% CaO which much exceeds the amount of alkali equivalent to the excess silica estimated from the chemical composition of the original acid clay.

Curing Property: Owing to the remarkable adsorptivity¹⁾ of the original acid clay, hard clay **N** tends to show a slow cure rate resulting in the poor reinforcing properties of the vulcanizates, which is attributable to the residual adsorptivity in the prepared filler. The 8 min vulcanizates containing the fillers treated with CaO less than 10% followed by calcination at 400 or 600 °C for 1.5 hr gave modulus and hardness lower than those of the 12 or 16 min vulcanizates (Table 2, No. 7, 10, 11, and 13). Treatment with CaO more than 10% and by calcination at 800 °C for 1 hr afforded the compounds normal cure. However, the formation of agglomerates, which were too hard to be disintegrated into sufficiently fine particles to give the desired strength, was unavoidable. Though the best sample (CaO 6%; calcination 600 °C, 1.5 hr; wet milling 18 hr) exhibited comparable tensile strength and higher elongation than those of Dixie Clay, its modulus was lower than that of the latter. Addition of some glycols or amines in the compounding may be expected to improve the lower modulus and tensile strength as well as the curing property like silica loading.²⁾

B. Preparation and Reinforcing Properties of Hard Clay ***M***: The preparation of good hard clay from **M** according to the same treatment with hydrated lime (3—60% CaO) and by subsequent calcination (400—800 °C, 1—1.5 hr) as mentioned above revealed that the optimum conditions were very close to those for **N**; the requisite amount of CaO lay in less than 10% and the calcination at 600 °C for 1.5 hr. Consequently **M** was treated with a less amount of CaO (1.25, 3, 6, or 9%) and then either calcined at 600 °C for 1.5 hr or dried at 110 °C for 5 hr in order to remove the moisture without calcination. Table 3 shows the reinforcing effects of the prepared fillers on SBR-1502 and Figs. 2 (a)—(d) demonstrate the results obtained under the optimum vulcanizing conditions.

Of all the fillers prepared from **M**, the one obtained with 3% CaO followed by calcination at 600 °C for 1.5 hr gave the loaded compound a maximum tensile strength comparable to that of Dixie Clay (Fig. 2-(a)). Although elongation 12% lower than that of Dixie Clay was observed, the modulus (300%) and hardness exceeded those of the reference filler by 52 and 14%,

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2) Y. Hirata, "Science of New Industrial Materials for Rubber," A-4, ed. by T. Kuwata, Kanehara Publishing Co., Ltd., Tokyo, (1941), Chap. VI, p. 179.

respectively (Figs. 2 (b)—(d)). The increase in alkali above the optimum amount gave rise to a slow decrease in both tensile strength and elongation. The decrease in alkali gave an abrupt diminution in the reinforcing properties. However, nearly constant modulus (300%) and hardness were obtained irrespective of the variation in alkali. A remarkable difference in the reinforcement of SBR-1502 was found between the fillers calcined at 600 °C for 1.5 hr and those only dried at 110 °C for 5 hr without calcination. In spite of the relatively high elongation of the latter, the modulus and the hardness were lower than those of the former. Even the highest tensile strength at 9% CaO was found to be less than a 60% value of Dixie Clay. Investigations by DPG adsorption test and electron microscopy revealed that the noticeably low reinforcing properties could be attributed to the surface activity remaining in the filler, which causes the fine particles disintegrated in wet state to recondense into aggregates during the course of drying.

The optimum conditions can be concluded to be as follows. The optimum amount of quicklime is 3% for **M** and 6% for **N**; calcination at 600 °C for 1.5 hr. Variation in the optimum amount of alkali can be ascribed to the difference of the mineralogical constituents of the specimens, especially to the presence of abnormal montmorillonite, because it exhibits much greater adsorptivity and requires a greater amount of alkali than in normal one. The pulverized products thus prepared give the SBR-1502 compounds excellent reinforcing properties comparable to those of Dixie Clay.

C. Effects of Mixing, Disintegration, and Sieving: **M** (150 g) and quicklime (8.02 g, 6% CaO) were mixed for 1 hr manually with a mortar and pestle into a paste with 100 ml water (procedure M) or mechanically with a porcelain ball mill in slurry (procedure B).[1] After drying the mixture obtained by procedure M at 110 °C, the dried matter was calcined at 600 °C for 1.5 hr. The resulting product was ground by means of wet ball-milling for 6, 12, 18, or 24 hr. On being filtered off, the ground particles were dried again at

TABLE 4. EFFECTS OF MIXING, DISINTEGRATION, AND SIEVING IN THE PREPARARION OF HARD CLAY **M** ON THE REINFORCEMENT OF SBR-1502

Run No.	Mixing		Pulverization		Sieving[d)]	Vulcanization time, min	Tensile strength kg/cm²	300% Modulus kg/cm²	Elongation %	Hardness JIS
	CaO (%)	Mode[a)]	Mode[b)]	Time[c)] hr						
1	6	M_1	B_W	6	—	8	70.0	31.3	708	63
						12	74.2	33.2	718	64
						16	77.3	32.2	719	63
2	6	M_1	B_W	12	—	8	82.7	31.6	712	64
						12	81.0	33.0	700	64
						16	83.1	32.8	720	64
3	6	M_1	B_W	18	—	8	88.5	32.4	678	65
						12	83.5	34.0	661	65
						16	88.3	33.1	690	65
4	6	M_1	B_W	24	—	8	81.9	42.5	536	67
						12	83.2	43.7	508	67
						16	80.7	43.3	551	67
5	6	B_1	B_W	18	W_{300}	8	86.8	35.9	667	65
						12	93.7	42.0	627	68
						16	91.9	39.9	660	68
6	3	B_1	B_W	18	W_{300}	8	94.2	35.4	793	62
						12	95.8	43.2	661	66
						16	100.1	41.4	688	66
7	6	B_1	A_d	2*	—	8	14.3	11.0	549	56
						12	16.6	11.5	657	59
						16	18.7	12.9	794	62
8	6	B_1	A_d	2*	D_{200}	8	17.3	14.1	717	58
						12	18.0	11.9	794	59
						16	18.4	11.6	855	60
9	Dixie Clay, reference filler					8	97.1	25.1	802	56
						12	102.6	27.3	782	58
						16	90.8	27.8	715	60

a) M_1 and B_1 denote manual or mechanical mixing of raw materials for 1 hr respectively with a mortar and pestle and with a ball mill.

b) B_w and A_d denote pulveriztion of the calcined matter by wet ball-milling and with an atmoizer in dry state, respectively.

c) W_{300} and D_{200} denote sieving of the pulverized product with a 300 mesh standard sieve (JIS) in wet state and with a 200 mesh in dry state, respectively.

d) 2* indicates pulverization repeated twice.

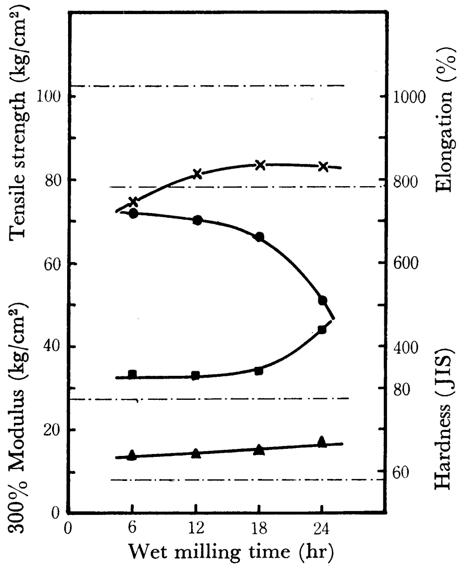

Fig. 3. Effects of wet ball-milling time in the preparation of **M** hard clay on the maximum reinforcement of SBR-1502 as compared with that of Dixie Clay.
×—× tensile strength (kg/cm²); ■—■ 300% modulus (kg/cm²); ●—● elongation (%); ▲—▲ hardness; ----- Dixie Clay

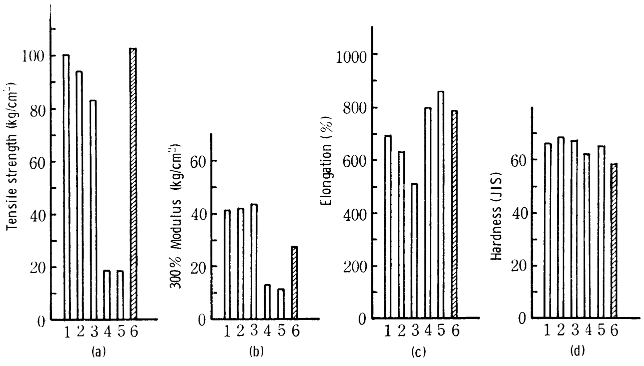

Fig. 4. Effect of admixing, pulverization, and sieving in the preparation of **M** hard clay on the reinforcement of SBR-1502 as compared with that of Dixie Clay.

Sample No.	Admixing		Pulverization		Sieving
	CaO %	Mode	Mode	Time, hr	
1	3	B_1	B_W	18	W_{300}
2	6	B_1	B_W	18	W_{300}
3	6	M_1	B_W	18	—
4	6	B_1	A_d	2*	—
5	6	B_1	A_d	2*	D_{200}
6 Dixie Clay, reference filler					

110 °C followed by pulverization with an atomizer (Table 4, Runs 1—4). Two samples mixed with alkali (3 and 6% CaO) by procedure B were prepared similarly by subsequent drying, calcination and wet ball-milling for 18 hr. In order to remove coarser particles, the disintegrated product was diluted with water to about 10% slurry and then made to pass through a 300 mesh standard sieve (JIS). Sieving after the milling for 18 hr, however, was found to be unnecessary. On being dried at 110 °C, the dehydrated product was pulverized with an atomizer to give a reinforcing filler (Table 4, Runs 5 and 6). Two more specimens mixed with alkali (6% CaO) by procedure B were obtained by the same treatment as above. Both calcined matters were disintegrated repeatedly in dry state with the atomizer. One of them was made to pass through a 200 mesh sieve before the compounding tests (Table 4, Run 8). The effects of the fillers thus prepared on the reinforcement of SBR-1502 were examined in comparison with those of Dixie Clay (Table 4). The results obtained under the optimum vulcanizing conditions are given in Figs. 3 and 4 (a)—(d).

So far as the calcined matter is concerned, the longer the wet milling time, the finer the resulting disintegrated particles. As disintegration proceeds sufficiently, a greater increase in the specific surface area contributes to a noticeable increase in the reinforcing capacity of the filler. The compound loading the filler, consequently, exhibited a considerable increase in tensile strength, modulus and hardness, accompanied by a remarkable decrease in the elongation as well (Fig. 3). The reinforcing properties were strictly or nearly in proportion to the wet milling time up to about 18 hr, and then approached a saturated value in the tensile strength or abrupt changes in the modulus (300%) and elongation. Both modulus and hardness far exceeded those of Dixie Clay, but the tensile strength and the elongation still fell short of the reference filler. This can be explained in terms of the effect of heterogeneous, manual mixing of the raw materials by procedure M as compared with the specimen (Table 3, No. 7) prepared by procedure B or mechanical mixing. A distinguishable difference in the reinforcing character between the fillers prepared by procedures B and M is ascribable to the high efficiency of the mechanical disintegration in mixing the raw materials (Table 4, Runs 3 and 5). Procedure B with a ball mill gives a homogeneous mixture leading to the promotion of the Pozzolanic reaction[3] between the acid clay and hydrated lime, which causes the formation of calcium montmorillonite as well as calcium silicate hydrates with the excess silica involved. As a result, the subsequent calcination proceeds so uniformly that any local sintering due to the polycondensation of acid clay itself can be avoided effectively. This should facilitate the pulverization of the calcined matter and contribute to the production of a better reinforcing filler.

The effect of sieving after the disintegration of calcined matter in dry or even in wet state on the reinforcing properties of the prepared filler was found to be relatively small or negligible as compared with that induced by the difference in procedure of mixing

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[3] a) S. Diamond, J. L. White, and W. L. Dolch, "Clay and Clay Minerals, Proc." 12th Natl. Conf., Pargamon Press, New York, N.Y. (1964), p. 359; b) C. G. Ruff and C. Ho, *High Way Research Board Bulletin*, (139), 42 (1966); c) G. R. Glenn and R. L. Handy, *ibid.*, (29), 70 (1963); d) C. Ho and R. L. Handy, *ibid.*, (29), 55 (1963); e) G. H. Hilt and D. T. Davidson, *ibid.*, (304). 51 (1961); f) J. L. Eades and R. E. Grim, *ibid.*, (262), 51 (1960); g) A. Ariizumi, "Advances in Clay Science," Vol. V, ed. by H. Minato, Clay Sci. Soc. Japan, Gihodo, Tokyo (1965), p. 219; h) R. Turriziani, "The Chemistry of Cements," Vol. 2, ed. by H. F. W. Taylor, Academic Press Inc., New York, N.Y. (1964), p. 69; i) W. Eitel, "The Physical Chemistry of the Silicates," Univ. Chicago Press, Chicago, (1954), III, p. 1255.

Table 5. Difference in reinforcing character due to loading amount between hard clay **M** (CaO 3%; calcination 600°C, 1.5 hr; wet milling 18 hr) and Dixie Clay

Exp. no.	Reinforcing filler Variety	Reinforcing filler PHR	Vulcanization time, min	Tensile strength kg/cm²	300% Modulus kg/cm²	Elongation %	Hardness JIS
1	Blank	0	8	8.5	6.6	353	33
			12	8.1	6.8	242	40
			16	7.0	6.4	194	41
2	Hard clay **M**	50	8	89.8	12.3	921	43
			12	89.5	12.3	903	45
			16	97.5	12.7	905	45
3	Hard clay **M**	100	8	86.8	35.9	667	65
			12	93.7	42.0	627	68
			16	91.9	39.9	660	68
4	Hard clay **M**	150	8	85.4	60.0	346	87
			12	83.9	70.0	341	88
			16	84.3	70.0	329	88
5	Dixie Clay	50	8	57.4	15.0	827	48
			12	74.8	18.0	787	50
			16	72.9	18.7	751	51
6	Dixie Clay	100	8	97.1	25.1	802	56
			12	102.6	27.3	783	58
			16	90.8	27.8	715	60
7	Dixie Clay	150	8	53.2	34.8	460	56
			12	77.4	40.5	561	62
			16	91.4	46.5	574	65

and disintegration as well as the applied amount of alkali.

Thus pulverization of the calcined matters and the mixing of the raw materials are indispensable. Even if proper conditions are selected for treatment with lime and calcination as well as the raw materials, the filler prepared without being disintegrated sufficiently would not exhibit the maximum reinforcement of the elastomer. The reinforcement of an elastomer by loading inorganic fillers is caused by the interaction[4] between the filler and the elastomer. The greater the specific, effective surface area of the filler applied, *i.e.*, the smaller the fineness of the filler pulverized, the greater the reinforcing effects with a given amount of the prepared filler on the elastomer would be expected. Pulverization, therefore, is considered to be the most important process for the calcined matter and comprises a significant factor dominating the reinforcing character of the final product. From the viewpoint of the high efficiency of disintegrating the calcined matters, wet milling with a porcelain ball mill is more suitable than dry pulverization with an atomizer alone, and is considered to be indispensable for this purpose. Owing to its poor efficiency, the reinforcing properties of the fillers pulverized by the atomizer were hardly expect-

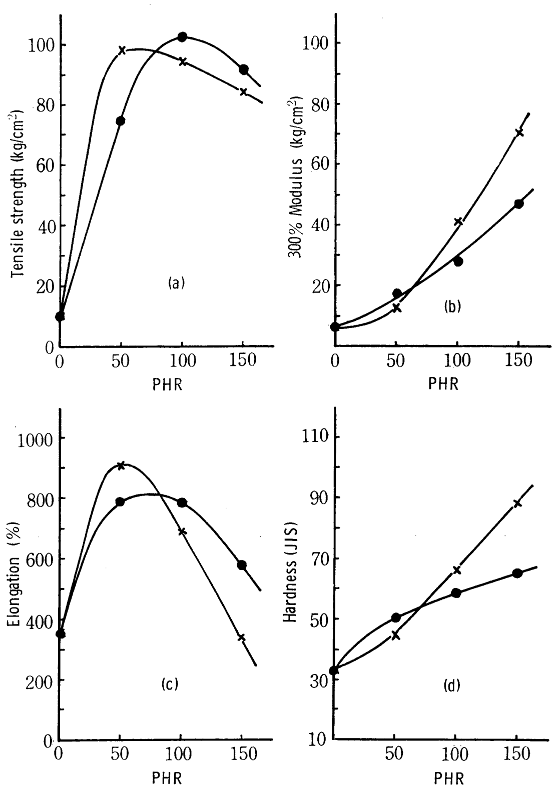

Fig. 5. Difference in reinforcing properties due to the loading amount between Dixie Clay and **M** hard clay (CaO 3%; calcination 600 °C, 1.5 hr; wet milling 18 hr).
×—× **M** hard clay; ●—● Dixie Clay

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able. Regardless of the relatively high elongation and hardness observable in the loaded compounds, the tensile strength and modulus were only 20—30% as low as those of Dixie Clay (Figs. 4 (a)—(d)).

D. Variable Loading Test with Hard Clay M: For investigating the difference in the reinforcing properties between Dixie Clay and the best filler obtained, hard clay **M** prepared under the optimum conditions (CaO 3%; calcination 600 °C, 1.5 hr; wet milling 18 hr) was subjected to a variable loading test with SBR-1502 ranging 0, 50, 100, and 150 PHR in weight (Table 5). Figures 5 (a)—(d) give the results obtained under the optimum vulcanizing conditions.

It is evident that the reinforcement with the prepared hard clay is comparable to that with Dixie Clay. However, some differences can be seen in the maximum reinforcement of the elastomer; hard clay **M** exhibits it around 50 PHR, Dixie Clay around 100 PHR. The former thus undergoes a greater change due to the loading amount than the latter. The deviation seems to be attributable to the particle size as well as morphological, structural, and physicochemical properties originating from the mineralogical constituents of the fillers.

Curing Property: All samples of hard clay **M**, even the one treated with minor alkali (CaO 1.25%) and dried at 110 °C for 5 hr without calcination, showed no such delay of cure as hard clay **N**, and gave higher reinforcing properties than those of the latter treated with the corresponding conditions (Table 3). The best sample (CaO 3%; calcination 600 °C, 1.5 hr; wet milling 18 hr) showed favorable reinforcing properties in tensile strength, modulus, and hardness which were equivalent or even higher than those of Dixie Clay in the tested range. The elongation was somewhat higher at lower loading than 75 PHR and a little lower at higher loading than those of the reference filler, the maximum reinforcement being observable for the low ratio, 50 PHR (Fig. 5).

Evaluation of Reinforcing Properties: From a practical viewpoint, white fillers with high modulus and hardness are useful. If the tensile strength of vulcanizates as well as the recipe and vulcanizability of compounds were equivalent, the higher modulus given by a filler is considered to be a measure of the greater reinforcing capacity.[5] In a variable loading test, such a filler exhibits the maximum tensile strength at a relatively low ratio. Though negative effects of the filler on the tear resistance and flexing life of the vulcanizate are inevitable, better abrasion resistance can be expected as well. In case of hard clay **M**, however, the negative effects are assumed to be relatively small because of the less diminution of elongation and tensile strength in the variable loading test in spite of the high modulus and hardness.

Consequently hard clay **M** might excel as a reference filler in its reinforcing properties such as modulus, hardness, and abrasion resistance.

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