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Preparation of Reinforcing Fillers from Japanese Acid Clays with Lime and by Calcination. I. Availability of Raw Materials for Preparing Hard Clay and the Properties of Products

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Reinforcing fillers for elastomers were prepared from three representative specimens of Japanese acid clay by treatment with hydrated lime (CaO 10%), subsequent calcination (600°C, 1.5 hr), and mechanical disintegration. Physicochemical properties of the products such as hygroscopicity, pH, diphenylguanidine (DPG) adsorption, specific gravity, and bulk density were determined in comparison with those of raw materials. Morphological and structural features were investigated by means of electron microscopy, X-ray diffraction, infrared and far infrared spectroscopy, DTA, and TGA. The reinforcing effects on SBR-1502 were compared with those of Dixie Clay and Silene EF. The following results were obtained. (1) Acid clays containing montmorillonite and α-cristobalite as principal constituents are suitable for the preparation of the fillers, but not the clay containing halloysite mineral as a major component in the randomly mixed-layers of kaolinite and montmorillonite with no excess silica. (2) Irreversible contraction as well as the formation of calcium silicates took place in montmorillonite minerals. Calcium silicate is formed in two states, one covering the surface of montmorillonite minerals and the other being set free. This gives rise to remarkable changes in adsorptivity, pH, swelling, bulk density, and specific gravity. Thus it becomes possible to use acid clays as reinforcing fillers. Hygroscopicity and the pH could be made about the same as those of Silene EF. The DPG adsorption capacities could be reduced as low as that of Dixie Clay. The products thus obtained greatly increased in bulk density and exhibited an average property of Dixie Clay and Silene EF in reinforcing SBR-1502.

Elastomer reinforcement with inorganic fillers seems to be influenced by their properties. Specific surface area and the available functional groups of the filler play the most important role.1–3)

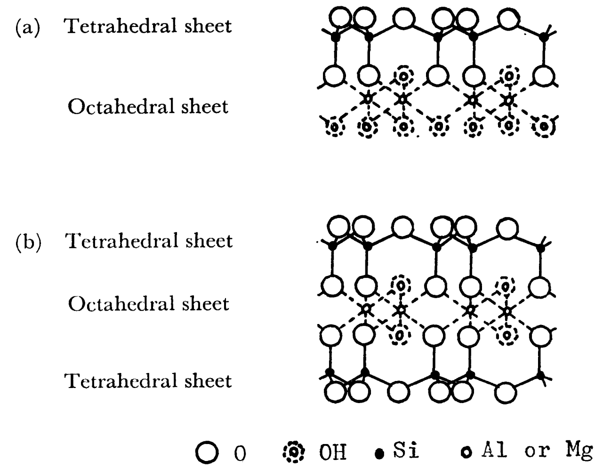

Fig. 1. Base structures of a two-sheet mineral (a) and a three-sheet mineral (b) (schematic).

Kaolinite is composed of a hydrated aluminum silicate with a two-layer type sheet structure as shown in Fig. 1-(a). Reinforcement of elastomers with kaolinite has been attributed to the effective hydroxyl groups of the external crystal surfaces and the fineness.4)

Since kaolinite resource is small in Japan, we have attempted to prepare a reinforcing filler such as hard clay from Japanese acid clays. Acid clays generally contain montmorillonite minerals of three-layer type sheet structure as shown in Fig. 1-(b) accompanying some hydrous amorphous silica.5) Their primary particles are finer than those of kaolinite.6)

In view of the similarity in the constitutional units, fineness and functional groups between montmorillonite and kaolinite, the acid clays can be used as a material of reinforcing fillers. However, the structural factors5c,7) such as substitutions in the tetrahedral and/or octahedral sheet, nonconformity in the layers, and lattice defects of montmorillonite give rise to too great adsorption, cation exchange, swelling, and catalytic activity.

If such surface activity could be controlled keeping fineness and effective hydroxyl groups unchanged, acid clays can be transformed into hard clay. Attempts were made from this viewpoint. Thermal treatment caused dehydroxylation as well as dehydration. Dehydroxylation gave rise not only to an irreversible contraction but also the polycondensation in the interlayers, reducing the adsorptivity noticeably. Caking or sintering of the minute particles which took place during the course of thermal treatment made it difficult for the products to be disintegrated mechanically or rehydroxylated even in wet milling. Thermal treat-

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1) S. Yamashita, *Kogyo Kagaku Zasshi*, **73**, 50 (1970).

2) G. Kraus, *Rubber Chem. Technol.*, **38**, 1070 (1965).

3) E. Suito, *J. Soc. Rubber Ind. Japan*, **34**, 441 (1962).

4) E. Suito and M. Arakawa, *ibid*, **36**, 704 (1963); *Kogyo Kagaku Zasshi*, **66**, 1616 (1963).

5) a) T. Mitsuda, *J. Mineral. Soc. Japan*, **4**, 342, 359 (1960); b) T. Sudo, "Mineralogical Study on Clays of Japan," Maruzen Co., Tokyo (1959), p. 194; c) Y. Otsubo, *Kagaku To Kogyo*, **4**, 229 (1951).

6) a) R. E. Grim, "Clay Mineralogy," 2nd Edt., MacGraw-Hill Ind. (1968), p. 165; b) E.C. Jonas and R.M. Oliber, "Proceedings of the 15th National Conference for Clay and Clay Minerals," Pergamon Press, New York (1967), p. 27.

7) R. E. Grim, Ref. 6a, p. 77.

TABLE 1. CHARACTERISTICS OF ACID CLAYS

Sample	Symbol	Mineralogical composition	Structural formula	Excess silica	Locality
Kuramitsu acid clay	**K**	More halloysite than montmorillonite in randomly mixed layers	$(Al_{1.60}Fe_{0.13}Mg_{0.26})(Si_4)$ - $O_{10}(OH)_2X_{0.33}$	<1%	Kuramitsu, Sugaya-mura, Kitakambara-gun, Niigata Prefecture
Matsune acid clay	**M**	Normal montmorillonite, only	$(Al_{1.48}Fe_{0.06}Mg_{0.50})(Si_4)$ - $O_{10}(OH)_2X_{0.33}$ - $3.36\ SiO_2\ 0.31\ H_2O$	34	Matsune, Kushibiki-mura, Higashitagawa-gun, Yamagata Prefecture
Nakajo acid clay	**N**	More abnormal montmorillonite than normal one	$(Al_{1.35}Fe_{0.15}Mg_{0.55})(Si_4)$ - $O_{10}(OH)_2X_{0.33}$ - $0.08\ SiO_2\ 0.48\ H_2O$	13	Nakajo-machi, Kitakambara-gun, Niigata Prefecture

ment diminished markedly the reinforcing effects of the fillers. Treatment with alkali only afforded alkali-montmorillonites and hydrous alkali silicates which still showed considerable rehydration. The surface activity did not decrease satisfactorily. Caking which took place on drying made it difficult for particles to be pulverized. The residual alkali caused an early scorching of loaded compound and poor aging resistance of the vulcanizate.

Treatment with a proper alkali such as hydrated lime and subsequent calcination caused the fixation of the applied cation in the cavities of the tetrahedral sheets as well as an irreversible contraction. Formation of calcium silicates with excess silica, covering external and internal surfaces of the montmorillonite crystallites or existing in an isolated state, improve the properties.

This paper describes the preliminary results on the preparation of reinforcing fillers from acid clays. Three representative specimens of acid clays, Nakajo (**N**), Matsune (**M**), and Kuramitsu (**K**) were first treated with lime (CaO 10%) and then calcined at 600°C for 1.5 hr. Their physicochemical properties such as hygroscopicity, pH, DPG adsorption, specific gravity, and bulk density were determined. The mineralogical features were investigated by means of electron microscopy, X-ray diffraction, infrared and far infrared spectroscopy, DTA, and TGA. The reinforcing effects on SBR-1502 were examined in comparison with those of Dixie Clay and Silene EF. Availability of the acid clays as a raw material for hard clay was discussed.

Experimental

Raw Materials. *Acid Clays*: Specimens from Mizusawa Chem. Ind. Co. were used (Table 1). Five kilograms of the air dried, massive specimens[8] of light yellowish gray (**N**) consisting of montmorillonites (the amount of abnormal montmorillonite is greater than that of normal one) containing excess silica (13%) were crushed in an iron mortar, sifted through a 6 mesh screen of Tylor standard sieves and then subjected to homogeneous mixing. The white powdery (**M**) consisting only of normal montmorillonite containing excess silica (34%) and light yellowish gray (**K**) containing halloysite as a major component in the randomly mixed-layers of kaolinite and montmorillonite with no excess silica were also studied.

Quick Lime: Calcium oxide of reagent grade with grain sizes 10—30 cm^3 was pulverized and grains smaller than 60 mesh were chosen.

Preparation of Reinforcing Fillers. Acid clay (150 g), water (1000 m*l*), and quick lime (CaO, 10% in wt. of the acid clay dehydrated at 110°C for 4 hr) were put into a porcelain ball mill of about 3 *l* containing 2 kg of porcelain balls of diameter 10 mm, and ground at 40 rpm for 1 hr at room temperature. The slurry of acid clay was filtered, dried at 110°C, and calcined at 600°C for 1.5 hr. The resulting product was subjected to wet milling at 40 rpm for 18 hr at room temperature. It was then diluted with water to about 10% slurry and passed through a 200 mesh sieve to remove coarse particles. After the finer particles obtained by filtration were dried at 110°C, the dehydrated product was pulverized with an atomizer.

Determination of Physicochemical Properties. The following properties were studied.

Hygroscopicity: One gram of the specimen which had been exposed to the air for 24 hr at room temperature was taken into a 10 m*l* weighing bottle and dried at 110°C in an electric oven to a constant weight. The loss in weight (%) before and after drying was determined as a measure of hygroscopicity.

pH: The value was determined by the JIS K 6221 (1960) method[9] with a pH meter with a glass electrode.

DPG adsorption: The adsorptivity for vulcanizing accelerator was estimated by means of a method which is a modification of the one for carbon black.[10] Reagents were prepared as follows: (a) 0.01 N DPG ethanol solution. DPG (2.11 g) was dissolved in 1 *l* of ethanol (purity 99.7%) followed by filtration. (b) Bromophenol blue (BPB). 0.1% ethanol solution was prepared for the use as an indicator. Estimation of DPG adsorption was carried out as follows: Two grams of the specimen dried at 110°C for 3 hr just before assay was taken into a 200 m*l* conical flask with a stopper. After addition of 100 m*l* of the 0.01 N DPG ethanol solution the flask was closed and the following treatment was carried out 5 times: Shaking of the flask for 1 min and then putting it to stand for 5 min. The resulting mixture was centrifuged for 10 min at 3000—3500 rpm. Ten milliliters of the supernatant liquid was then taken for titration with a 0.01 N HCl standard solution in the presence of 3 drops of the BPB ethanol solution. The original blue solution turned green at the end of titration. Blank tests were carried out simultaneously. The amount S of the DPG adsorbed by 10 kg of the dehydrated filler was estimated by the following equation from the average of two measurements for each specimen.

$$S = \frac{211 \cdot f \cdot (B-C)}{W} \times 10^4$$

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[8] grain size, *ca.* 30—120 cm^3.

[9] Japanese Industrial Standards (JIS) K 6221-60 (1960); American Standards for Testing Materials (ASTM) D 1512-57T (1957).

[10] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, **23**, 646 (1931).

where

f = factor of the 0.01 N HCl solution
B = volume (ml) of the 0.01 N HCl solution consumed in the blank test
C = volume (ml) of the 0.01 N HCl solution consumed in the test
W = weight (g) of the dehydrated filler applied
211 = molecular weight of DPG

Specific Gravity: One gram of the specimen was dried at 110°C for 2 hr, following the ASTM D 135-39 method A.[11] Kerosene (bp 70—100°C/2 mmHg) was used as an immersion liquid (D_4^{20} 0.7811).

Bulk Density: The measuring cylinder method[12] was applied.

Morphological and Structural Studies. The shape, size, and structural features both of the fillers and raw materials were investigated by means of electron microscopy, X-ray diffraction, infrared and far infrared spectroscopy, DTA, and TGA.

Electron Microscopy: Studies were carried out with a JEOL (Japan Electron Optics Laboratory Co.) JEM-6AS electron microscope operating at 50 kV.

X-Ray Diffraction: The patterns were obtained with a Rigaku Denki Geigerflex diffractometer using nickel filtered Cu-$K\alpha$ radiation, 30 kV, 12 mA, rate meter 16, multiplier 1, time constant 4 sec, slits 1°–1°–0.2 mm, scanning speed 2° (2θ)/min, chart speed 1 cm/min.

Infrared and Far Infrared Spectroscopy: Measurements were carried out with a JASCO Model DS-403G spectrophotometer through a KBr disc and Nujol mull in the regions 4000—200 and 4000—2800 cm^{-1}, respectively.

DTA and TGA. Thermal analyses were carried out with a Rigaku Denki Thermoflex differential thremogravimetric analyser up to 1300°C with a heating rate 10°C/min.

Structural formulas of the acid clays and the contents of excess silica were calculated by Otsubo's method[13] from the data of chemical analysis (Table 1).

TABLE 2. CONSTITUENTS (PHR) OF COMPOUNDS

SBR-1502	100	Vulcanizing accelerator, DM	1.5
Zinc oxide	5	Vulcanizing accelerator, TT	0.25
Sulfur	2	Antioxidant, D	1.0
Stearic acid	2	Reinforcing filler	75

Compounding Test. A master batch containing elastomer (SBR-1502), zinc oxide, sulfur, stearic acid, dibenzothiazoyle disulfide (DM), tetramethylthiuram disulfide (TT), and phenyl-β-naphthylamine (D) was loaded with the reinforcing filler and masticated with a test-roll (6″×8″, frontroll) under the following conditions: Number of revolution 17 rpm; speed ratio of the front and back rolls 1 : 1; roll temperature 55±5°C. The constituents of the compounds are given in Table 2. A test piece (diameter 70 mm, thickness 3 mm) was made from this compound by vulcanization at 150±3°C under a pressure of 1500 lb/in^2 for 8, 12, and 16 min and tested according to the JIS K 6301-62 (1962) method.[14] Tensile strength (kg/cm^2), modulus (300%, kg/cm^2) and elongation (%) were measured with a Schopper tensile tester. Hardness after 30 sec was determined with a spring tester. Data were taken from the average of four measurements. Values not reaching 80% of the maximum value were discarded. When one value is exceptional the average of the three measurements was taken. If two values are abnormal one 80% value is added to the normal ones. If three values are abnormal two 80% values are added.

Results

Physicochemical Properties. *Surface Properties*: The hygroscopicity of the fillers became less than half of that of the specimens. The adsorptivity for the DPG became smaller than 1/3—1/5 of the original values. The pH values 4.52—5.95 turned 9.80—8.45 (Fig. 2).

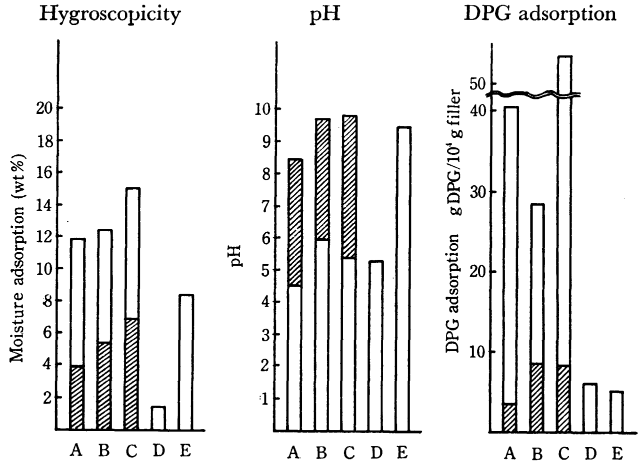

Fig. 2. Effect of treatment with lime (CaO 10%) and calcination (600°C, 1.5 hr) on hygroscopicity, pH, and DPG adsorption of the specimens in comparrison with those of Dixie Clay and Silene EF. Bar graphs indicate the results for original clays and reference fillers and hatched bars the prepared fillers.
A: Kuramitsu acid clay and **K** hard clay B: Matsune acid clay and **M** hard clay C: Nakajo acid clay and **N** hard clay D: Dixie Clay E: Silene EF

TABLE 3. SPECIFIC GRAVITY AND BULK DENSITY OF THE FILLERS IN COMPARISON WITH THOSE OF THE ORIGINAL ACID CLAYS AND REFERENCE FILLERS

Variety	Specific gravity		Bulk density
	Hard clay	Acid clay	cc/g
Kuramitsu-series	2.3946	2.4958	2.25
Matsune-series	2.2298	2.3891	3.02
Nakajo-series	2.3032	2.4755	2.54
Dixic Clay	2.5684	—	1.38
Silene EF	2.0989	—	4.05

Specific Gravity and Bulk Density: The maximum specific gravity of the specimens was in the order **K**<**N**<**M**. The prepared fillers showed the same order with 4—7% decrease in the values. The values of bulk density were also found to be in the same order **K**<**N**<**M**. This is in line with the amount of excess silica and the decrease in iron contents (**K** 2.93; **N** 2.75; **M** 0.79%) in the raw materials. The results agreed with the distribution observed by electron microscopy.

Morphological and Structural Features. *Morphological Studies*: *Shape and Size*: Hard clay **K** contains grains of maximum size, and hard clays **M** and **N**

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[11] ASTM D 153-39 (1939).

[12] S. Kuribayashi, "Methods of Examination for Rubber and Relating Materials," ed. by S. Kunisawa, Soc. Rubber Ind. Japan (1963), p. 651.

[13] Y. Otsubo, Ref. 5c, p. 231; *ibid.*, **2**, 258 (1949).

[14] JIS K 6301-62 (1962).

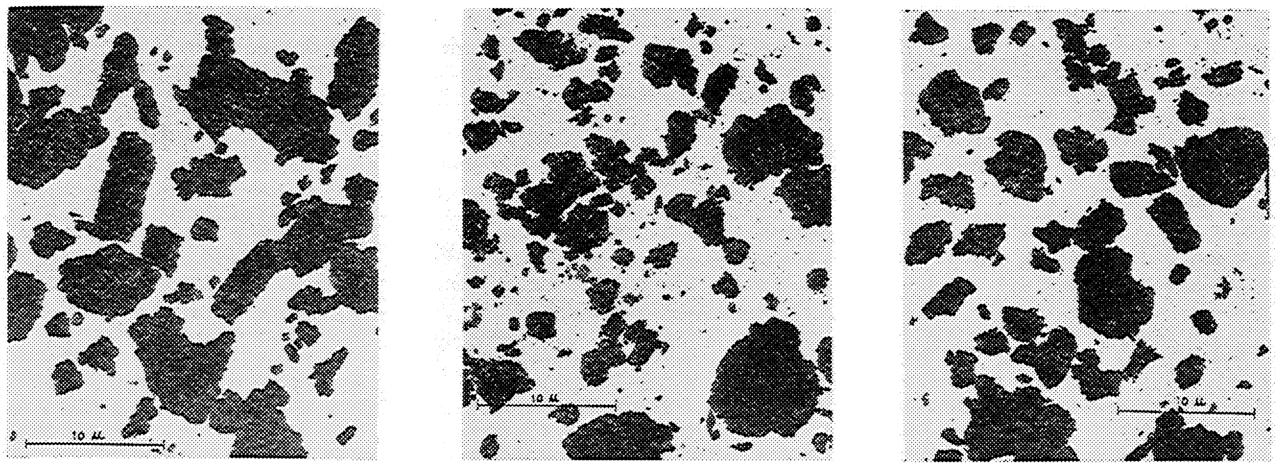

Plate 1: Kuramitsu acid clay ×4500 Plate 2: Matsune acid clay ×4500 Plate 3: Nakajo acid clay ×4500

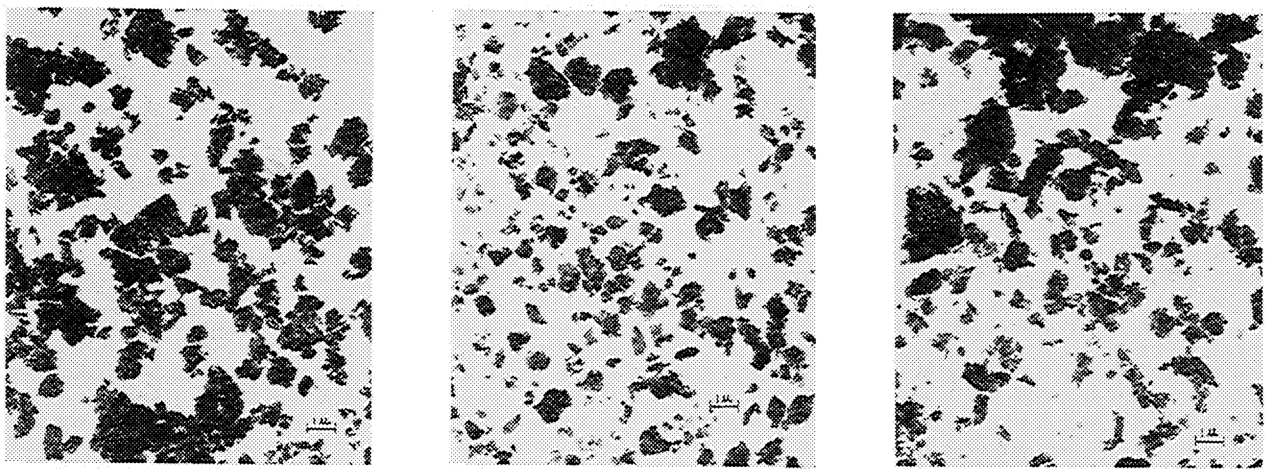

Plate 4: **K** hard clay ×9000 Plate 5: **M** hard clay ×9000 Plate 6: **N** hard clay ×9000

Fig. 3. Electron micrographs of the fillers (CaO 10%, calcined at 600°C for 1.5 hr) in comparison with those of original acid clays.

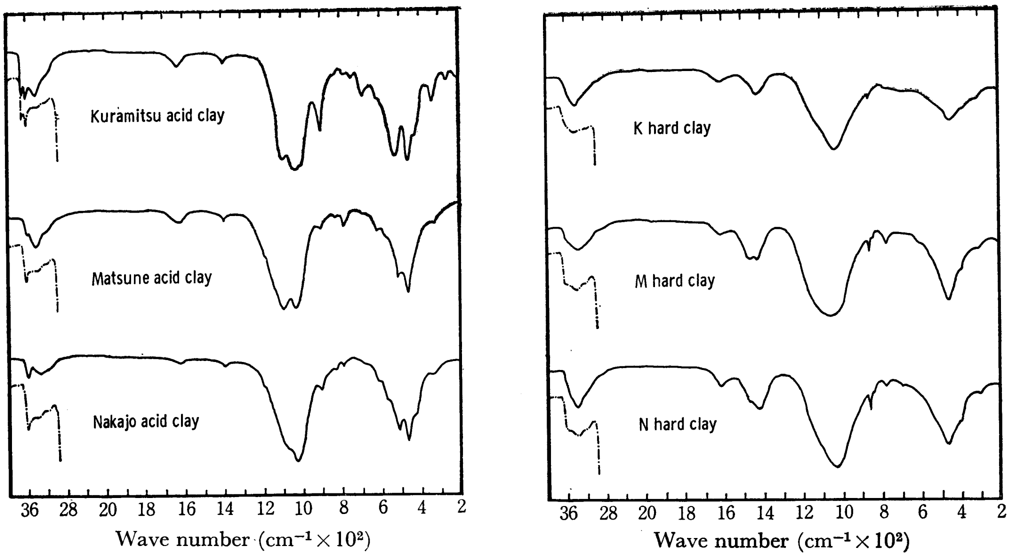

Fig. 4. Infrared and far infrared spectra of the fillers (CaO 10%, calcined at 600°C for 1.5 hr) in comparison with those of original acid clays.

contain small plate-shaped particles (Fig. 3). The grain size decrease with the increase of excess silica and the decrease of iron content.

New Minerals: A small amount of needle-like or cylindrical crystallites of calcium silicate hydrates[15] is contained in hard clays **M** and **N** but not in **K**. This was confirmed by selected-area electron diffraction. The less the content of excess silica, the less the formation of calcium silicate hydrates. However, the crystallites are large in size.

Investigation on Structural Features: *a) Infrared and Far Infrared Spectra*: The diagnostic bands[16] of montmorillonite in acid clays **M** and **N** changed with the treatment with lime and subsequent calcination as follows (Fig. 4). The bands around 3630 (νO–H, free), 3330—3420 (νO–H, hydrogen bonded), and 1630—1635 cm^{-1} (δO–H) diminished noticeably, and those around 913 (δAl^{3+}–O–H) and 838 cm^{-1} (δFe^{3+}–O–H) disappeared completely. Among the bands of layer-lattice silicates in the regions 900—1200 (νSi–O) and 400—650 cm^{-1}, the band around 1083—1100 cm^{-1} related to colloidal silica[17] and/or ion saturation[18] and the band 520 cm^{-1} related to (Si–O–Al$^{\text{VI}}$)[19] decreased markedly. The bands around 1033—1036 (νSi–O) and 470 cm^{-1} (δSi–O) related to the skeletal vibrations of the tetrahedrons of montmorillonite shifted towards higher frequencies overlapping the adjacent bands, giving one single, strong, and broader band around 1055 and 475 cm^{-1}, respectively. The band at 795 cm^{-1} (δSi–O, hydrated amorphous silica)[17] became broader with a slight diminution in intensity and a shift towards 791 cm^{-1}. The other weak bands at 617—621, 568—574, 431, 355, and 340 cm^{-1} characteristic of montmorillonite almost disappeared. New distinct bands ascribable to calcium silicate (1483—1472 and 858—856 cm^{-1})[20] and calcite (1435, 875, 715, and 318 cm^{-1})[21] appeared. The intensity of the former increased and that of the latter decreased with the increase in the amount of excess silica.

In the case of hard clay **K** the bands at 3714 (νO–H, free in the halloysite lattices),[16] 3638 (νO–H, free in the montmorillonite lattices),[16] 3434 (νO–H, hydrogen bonded) and 1630 cm^{-1} (δO–H) diminished markedly, while the bands of kandite minerals at 912 (Al^{3+}–O–H), 791 and 751 (Si–O–Al$^{\text{VI}}$, in-plane and perpendicular, respectively), 698 and 436 (δSi–O), 342 and 272 cm^{-1} disappeared completely. The prominent bands of skeletal vibrations at 1100, 1030, and 1010 (νSi–O), 541 (Si–O–Al$^{\text{VI}}$) and 470 cm^{-1} (δSi–O) similarly turned to single bands and became less prominent at 1046 and 467 cm^{-1}, respectively. These bands were much broader and markedly smaller than those of the original acid clay and the other hard clays **M** and **N**. Feeble absorption bands of calcium silicate (1472 cm^{-1}) and calcite (1434, 875, 715, and 319 cm^{-1}) were observed. This suggests that a considerable sintering of the minute crystallites as well as the collapse of the layer-lattices took place during the course of treatment.

b) DTA and TGA Thermograms: In the DTA

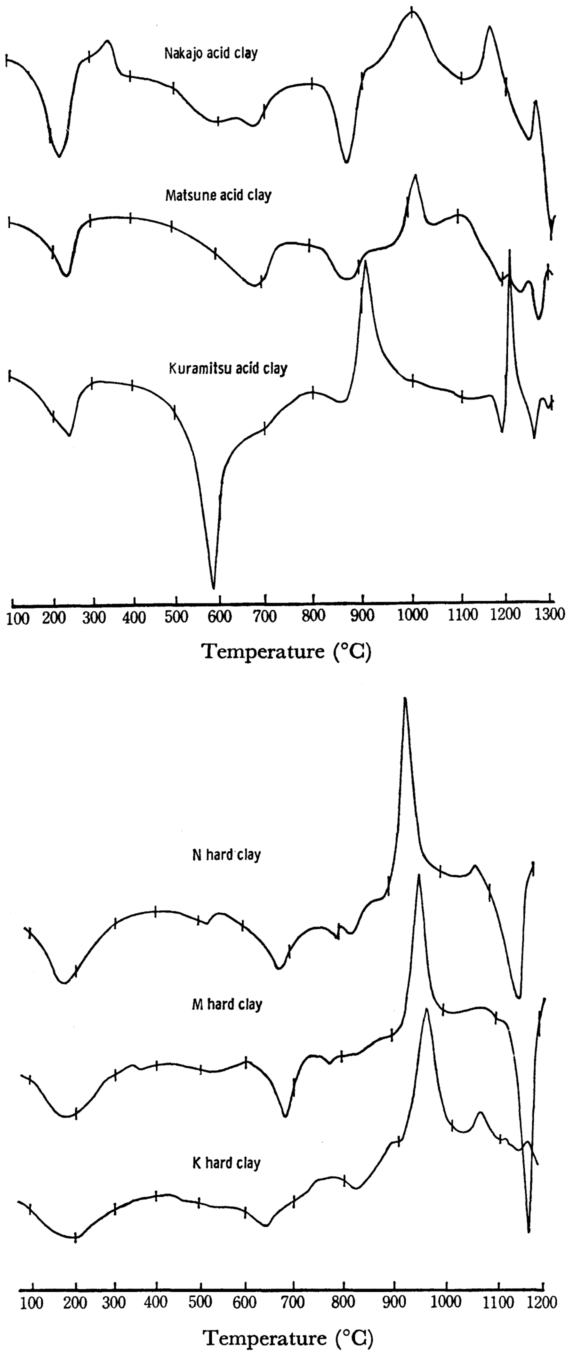

Fig. 5. DTA thermograms of the prepared fillers (CaO 10%, calcined at 600°C for 1.5 hr) in comparison with those of original acid clays.

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[15] a) J. A. Gard, "The Chemistry of Cement," Vol. 2, ed. by H. F. W. Taylor, Academic Press (1964), p. 256; b) H. F. W. Taylor, "Progress in Ceramic Sience," Vol. 1, ed. by J. E. Burke, Pergamon Press (1961), p. 89.

[16] I. Oinuma and H. Kodama, "Clay Science Handbook," ed. by S. Iwao, Clay Sci. Soc. Japan, Gihodo (1967), pp. 65—75.

[17] a) B. D. Mitchell, V. C. Farmer, and W. J. MacHardy, *Advan. Agr.*, **16**, 349 (1964); b) E. R. Lippincott, A. V. Valkenburg, C. E. Weir, and E. N. Bunting, *J. Res. Nat. Bur. Stand.*, **61**, 61 (1958); c) M. Field, I. K. Walker, and P. P. Williams, *New Zealand J. Sci. Tech.*, **38**, 31 (1956).

[18] V. C. Farmer and J. D. Russel, *Spectrochim. Acta*, **20**, 1149 (1964).

[19] V. Stubičan and R. Roy, *Z. Kristallogr.*, **115**, 200 (1961); *Amer. Mineral.*, **46**, 32 (1961).

[20] a) E. Suito and M. Arakawa, *J. Soc. Rubber Ind. Japan*, **34**, 885 (1961); b) K. Fukui, *ibid.*, **37**, 858 (1964).

[21] a) C. E. Weir and E. R. Lippincott, *J. Res. Nat. Bur. Stand.*, **65A**, 175 (1961); b) E. E. Angino, *Amer. Mineral.*, **52**, 137 (1967).

thermograms of the hard clays **M** and **N** prepared from the specimens containing montmorillonite and α-cristobalite as principal constituents, the diagnostic peaks of montmorillonite disappeared or diminished considerably (Fig. 5). Endothermic reactions: Dehydration (100—300°C, strong and sharp), dehydroxylation (500—750°C, strong and broad) and phase transition (820—910°C, strong or medium). Exothermic reactions: Oxidation of the organic matter adsorbed (around 350°C, medium), spinel or β-quartz (around 1000°C, strong and broad or sharp), β-cristobalite, mullite or cordierite (around 1150°C, medium). The fusion points of the specimens were observed to be around 1300°C and those of the fillers around 1170°C. Some new peaks appeared around 180 (due to the first endothermic reaction, very broad and strong), 678 (due to the second endothermic reaction, rather sharp and strong) and 930—950°C (due to the first exothermic reaction, very strong and sharp). They were attributed to calcium silicate hydrate.[23] No endothermic peak attributable to the decomposition of free alkali $Ca(OH)_2$ was found. However, a weak one ascribable to calcium carbonate[24] appeared around 795°C, suggesting the presence of a small amount of calcite. The amount estimated from the area of the endothermic peak was less than 3%. This seemed to decrease with the increase in the amount of excess silica.

In the case of hard clay **K** the characteristic peaks in the specimen also diminished or disappeared completely. Endothermic reaction: Dehydration (100—300°C, strong and broad), dehydroxylation of halloysite (586°C, very strong and sharp) and montmorillonite (around 695°C, strong and broad) and phase transition (855, 1190, and 1258°C, medium). Exothermic reaction: Phase transition related to halloysite (906 and 1208°C, very strong and sharp). The filler showed broad and strong endothermic peaks (195 and 639°C) and a relatively strong and sharp exothermic peak (953°C) which could be attributed to calcium silicate and aluminate, accompanied by several peaks (1053, 1109, and 1158°C).

The fillers exhibited similar profiles of TGA thermograms, which nearly corresponded to an intermediate of acid clay **M** and Silene EF. The former consists mainly of normal montmorillonite with excess silica, the latter being a hydrous calcium silicate (Fig. 6). The weight loss of hard clay **K** is greater than that of raw material. This suggests that dehydroxylation occurred to a greater extent during the course of calcination as compared with the rehydration during the course of wet milling. The weight loss of the other hard clays **M** and **N** decreased with the increase of the amount of excess silica in raw material due to the formation of hydrous calcium silicates.

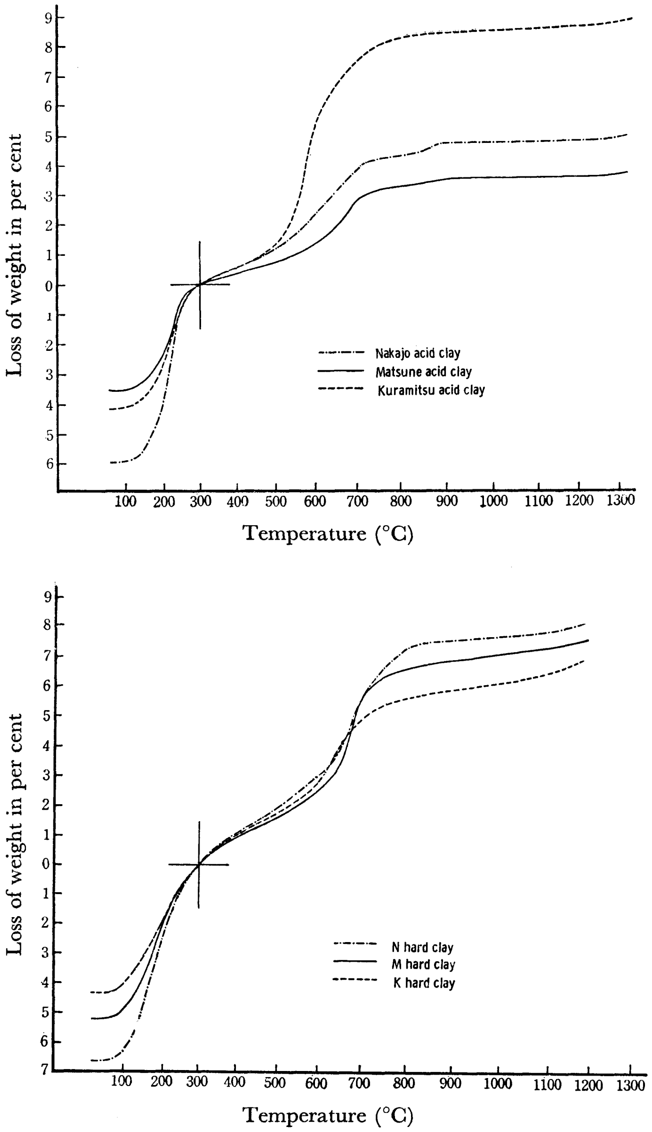

Fig. 6. TGA thermograms of the fillers (CaO 10%, calcined at 600°C for 1.5 hr) in comparison with those of original acid clays.

The results agreed with those of infrared and far infrared spectroscopy and X-ray diffraction.

c) X-Ray Powder Diffraction Patterns:[25] The treatment of the original acid clays with hydrated lime (CaO 10%) caused a slight shift from 15.4 to 13.7 Å in the basal reflections as a result of the formation of Ca-montmorillonite. The intensities of the prominent basal reflections related to the amounts of interlayer water did not change much. New reflections appeared which were ascribed to the calcium silicate hydrates (3.03 and 2.72 Å) which are very similar to Taylor's CSH[15b] and calcite (3.83, 3.03, 2.53, and 2.28 Å).[26] A slight decrease in the intensities of the α-cristobalite was observed as well. Subsequent calcination (600°C, 1.5 hr) caused an irreversible contraction along *c*-axis in the montmorillonite and the disappearance of basal

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22) a) R. G. Kelly, "The Differential Thermal Investigation of Clays," ed. by R. C. Mackenzie, Miner. Soc. London (1957), p. 140; b) R. E. Grim and Kulbicki, *Amer. Mineral.*, **46**, 1333 (1961).

23) S. Diamond, J. L. White, and W. L. Dolch, Caly and Clay Minerals, Proc. 12th Nat. Conf., Pergamon Press, New York (1964), p. 359.

24) a) S. Iwao ed., Ref. 15, p. 40, 395; b) R. C. Mackenzie ed., Ref. 22a, p. 331.

25) D.M.C. MacEwan, "The X-Ray Indentification and Crystal Structures of Clay Minerals," ed. by G. Brown, Miner. Soc. London (1961), p. 143.'

26) H. E. Swanson and R. K. Fuyat, *NBS Circular 539*, **II**, 51 (1953); ASTM, X-Ray Powder Data File Card 5-0586.

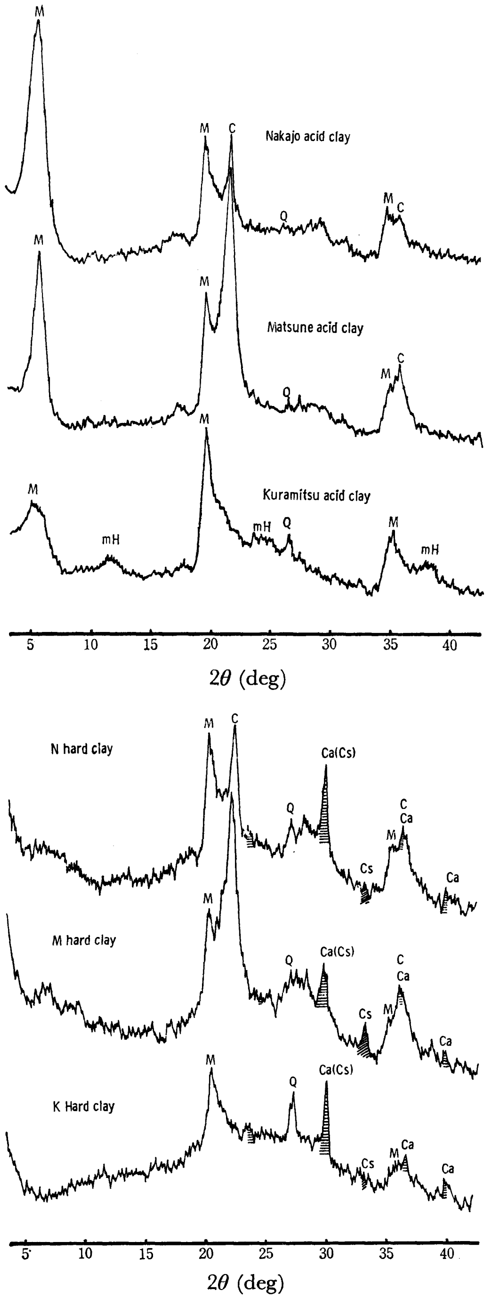

Fig. 7. X-ray powder diagrams of the prepared fillers (CaO 10%, calcined at 600°C for 1.5 hr) in comparison with those of their original acid clays. (Cu K_α radiation)
M: montmorillonite, mH: *meta*-halloysite, C: α-cristobalite, Q: quartz, Ca: calcite, Cs: calcium silicate hydrate

reflections. However, the crystal lattices remained with no serious collapse (Fig. 7). Amounts of calcium silicate hydrates and calcite estimated from the intensities of the X-ray reflections varied as follows. The former increased with an increase in the amount of excess silica α-cristobalite in raw material, and the latter decreased. This agreed with the results obtained for the structural features of fillers.

In hard clay **K** the distinct reflections of halloysite observable in the raw material disappeared almost completely, and those of montmorillonite diminished more markedly than in hard clays **M** and **N**. Only weak reflections of calcium silicate hydrate and calcite were observed together with that of unreacted quartz (3.34 Å).

Table 4. Reinforcing effects of the fillers on SBR-1502, derived from acid clays with lime (CaO 10%) and calcination (600°C, 1.5 hr)

Reinforcing filler	Vulcanization time, min	Tensile strength kg/cm^2	300% Modulus kg/cm^2	Elongation %	Hardness JIS
K hard clay	8	31.1	14.4	559	52
	12	34.9	13.9	559	52
	16	28.1	13.8	553	53
M hard clay	8	67.6	20.8	739	50
	12	59.4	20.9	732	52
	16	57.3	20.5	717	53
N hard clay	8	59.8	16.4	742	51
	12	59.3	16.4	726	52
	16	52.3	16.8	693	52
Silene EF	8	46.1	28.1	429	59
	12	50.7	26.7	486	61
	16	44.6	28.3	418	65
Dixie Clay	8	96.9	23.5	759	53
	12	93.0	25.3	720	55
	16	94.9	26.4	705	55

Reinforcing Effects on SBR-1502. The reinforcing effects of the fillers were compared with those of Dixie Clay and Silene EF (Table 4). The results obtained under the optimum vulcanizing conditions are given in Figs. 8 (a)—(b).

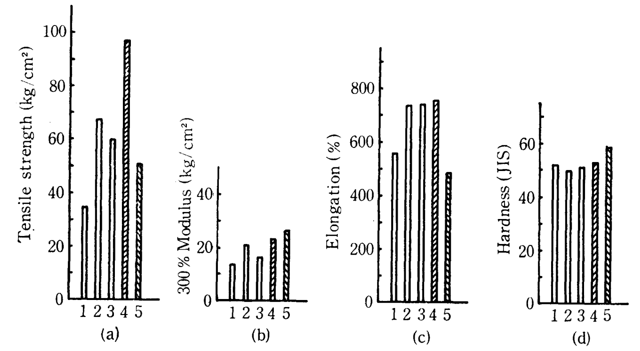

Fig. 8. Reinforcing effects of the prepared fillers (CaO 10%, calcined at 600°C for 1.5 hr) on SBR-1502 in comparison with those of Dixie Clay and Silene EF. Inscriptions are as follows:
(a): Tensile strength (kg/cm^2), (b): 300% Modulus (kg/cm^2)
(c): Elongation (%), (d): Hardness (JIS),
(1): **K** hard clay, (2): **M** hard clay, (3): **N** hard clay,
(4): Dixie Clay, (5): Silene EF

Tensile strength (kg/in^2): The compounds obtained by loading hard clay **M** or **N** exhibited 70% or a little less tensile strength than that of Dixie Clay (Fig. 8-a). It is much greater than that of Silene EF. In the case of hard clay **K** only 35% value of Dixie Clay or one half of hard clay **M** was obtained.

Modulus (300%, kg/in^2): The compounds obtained by loading the fillers gave lower modulus than those containing a reference filler Dixie Clay or Silene EF (Fig. 8-b).

Elongation (%): The compound obtained by loading the fillers exhibited fairly larger elongation as compared with those containing one of the reference fillers (Fig. 8(c)). Even the compound containing hard clay **K** showed much greater value than that of Silene EF. However, hardly any significant difference was observed between the compounds containing hard clay **M** and **N**.

Hardness: The compounds obtained by loading the fillers gave the hardness very close to that of Dixie Clay but smaller than that of Silene EF (Fig. 8-d).

The results show that the hard clays make the reinforcing effects on SBR-1502 increase with the increase in the amount of excess silica, the decrease in particle sizes, and the increase of the amount of remaining effective hydroxyl groups.

Discussion

The physicochemical and morphological studies on the fillers suggest that treatment with lime and subsequent calcination make the acid clays hydrophobic as well as basic. The fillers showed a noticeable diminution in their adsorptivity for the vulcanizing agent and moisture. Facility of crushing the products is closely related to both the mineralogical composition and the content of excess silica α-cristobalite.

Investigation of the structures of the fillers by X-ray diffraction, infrared and far infrared spectroscopy, and thermal analyses revealed the following. The above treatment caused an irreversible shrinkage along *c*-axis in montmorillonite as well as the formation of calcium silicate hydrates with the excess silica which covered the internal and external surfaces of the crystallites. This contributes in improving surface activity such as hygroscopicity, DPG adsorption capacity, swelling, and pH, and ease for the crushing of products. The formation of calcite is assumed to be originated from the carbonation of free alkali during the course of treatment.

Acid clay **K** containing halloysite as a major constituent in the randomly mixed-layers of kaolinite and montmorillonite with no excess silica, is considered to be more susceptible to treatment with lime and calcination than the acid clays **M** and **N** consisting mainly of normal and/or abnormal montmorillonites containing excess silica. This gives rise to an appreciable sintering as well as collapse in the layer lattices, which cause a glassification and caking of the minute crystallites or the primary particles due to the depression of fusion point by alkali treatment. The fact that hard clay **K** showed coarser particles, less bulk density, lower diminution in the specific gravity, greater decrease in the adsorptivity, and lower pH than those of the other two fillers **M** and **N**, can be attributed to its high susceptivility to the foregoing treatment.

The results on the reinforcement of SBR-1502 suggest that acid clays such as **M** or **N** can be used to prepare a reinforcing filler, but not an acid clay like **K**. Acid clay **M** (white) has the merit of providing a less colored product than that of acid clay **N** (light yellowish gray); the former contains less iron and more excess silica. The compound obtained by loading hard clay **M** gave much better reinforcing properties such as tensile strength, modulus, elongation, and hardness than that containing hard clay **N**. Thus acid clay **M** is considered to be a more suitable raw material.

Suito and Arakawa[4] reported on the reinforcing effects of hard clay on SBR-1502, a commercial reinforcing filler (kaolinite treated thermally up to 800°C). This suggests that the interaction between the hydroxyl radicals and the compounded elastomer molecules plays the most important role. The precise mechanism of the reinforcing effects has not been clarified. However, the markedly lower reinforcing effects of hard clay **K** as compared with those of the hard clays **M** and **N**, could be explained in terms of remarkable reduction of the specific surface area and the available hydroxyl groups.

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