Preparation of Reinforcing Fillers from Japanese Acid Clays with Lime and by Calcination. IV. Investigation on the Structure, Physicochemical Properties and Morphology of M Hard Clay in Relation to the Reinforcing Effect

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In order to find the optimum conditions for the preparation of satisfactory reinforcing filler from Matsune (**M**) acid clay, two series of fillers of **M** hard clay (CaO 0—9%: drying 110 °C, 5 hr for M-1 series; calcination 600 °C, 1.5 hr for M-2 series: wet ball-milling 6—24 hr) were investigated with respect to their structure, physicochemical properties and morphology. Treatment with hydrated lime (CaO 3%), followed by calcination (600 °C, 1.5 hr) and mechanical disintegration (wet ball-milling 18 hr) was found to give good results. Calcination after the lime treatment gives rise to adequate dehydroxylation as well as dehydration of the montmorillonite, calcium silicate hydrates (CSH) and excess silica remaining. This process helps to restrain the great surface activity of acid clay and facilitate pulverization of the final products combined with the effect of inhibiting polycondensation of the montmorillonite and α-cristobalite due to an even formation of the CSH distributed on the interlayer surfaces and the interfaces of the minute crystallites.

In previous papers we reported on the availability of Nakajo (**N**) and Matsune (**M**) acid clays for preparing a reinforcing filler of elastomers,[1] the optimum conditions of preparation and evaluation of their reinforcing properties.[2] An investigation of the changes in the structure, morphology and physicochemical properties of **N** hard clay derived from **N** with relation to the reinforcement was carried out.[3]

The same treatment as in **N** hard clay (CaO 3—60%; calcination 400—800 °C, 1.5 hr; wet ball-milling 18 hr) revealed that the optimum conditions for preparing a good hard clay from **M** were very close to those of **N**; the requisite amount of alkali less than 10% and calcination at 600 °C for 1.5 hr. The patterns of structural changes in **M** hard clay investigated by X-ray diffraction and IR spectroscopy were found to be similar to those of **N** hard clay. However, a deviation was accompanied by the optimum amount of alkali; 3% for **M** and 6% for **N**.

For the purpose of confirming the optimum conditions, **M** was treated with a less amount of hydrated lime (CaO 0—9%) and then either calcined at 600 °C for 1.5 hr or dried at 110 °C for 5 hr to remove the moisture. Changes in the structure, morphology and physicochemical properties of the fillers were examined as well.

Evidences are given to show the merit of the treatment with alkali followed by calcination and mechanical disintegration for the preparation of a satisfactory reinforcing filler from **M**.

Experimental

Materials. Two series of fillers of **M** hard clay (M-1 and M-2) were used; they were derived from Matsune acid clay with hydrated lime (CaO 0, 1.25, 3, 6 or 9%) followed by thermal treatment (drying 110 °C, 5 hr for M-1; calcination 600 °C, 1.5 hr for M-2) and mechanical disintegration (wet ball-milling 18 hr).[2]

Dixie Clay, Silene EF and the original acid clay **M** which had been ground under 200 mesh and dried at 110 °C for 2 hr without the lime treatment and mechanical disintegration beforehand were utilized as references.

Investigation on Structure, Physicochemical Properties and Morphology. The structure of **M** hard clay was investigated by X-ray diffraction, IR spectroscopy and thermal analyses, DTA and TG. The physicochemical properties were determined by means of hygroscopicity, pH, DPG adsorption, specific gravity and bulk density. The shape, size and particle distribution of the prepared fillers were studied by electron microscopy. The methods, apparatus and conditions of measurement are summarized in Table 1.

The structural feature of the best **M** hard clay (CaO 3%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr) was studied by selected area electron diffraction (SAD) technique in comparison with that of the best **N** hard clay (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).

Results and Discussion

Investigation of Structural Changes. (1) X-ray Diffraction Patterns. Figures 1 (a) and 1 (b) give the X-ray diffraction diagrams showing the difference of structural changes between the M-1 and M-2 fillers, respectively.

(i) M-1 fillers: As the amount of alkali increased, normal montmorillonite, the principal constituent of **M**, still retained its basal reflection[4] (15.37 Å) with a little diminution (less than 5%) in the intensity and a slight, constant shift (1.68 Å) towards a lower spacing (Fig. 1 (a) curves 1—5). The basal shift is smaller than in the case of **N** (about 2 Å) and attributable mainly to the formation of Ca-montmorillonite.

The intensity of α-cristobalite[5] (4.05 Å (101), the most prominent reflection characteristic of **M**, decreased in proportion to the amount of alkali. New but feeble reflections ascribable to tobermolite-like calcium silicate hydrates[6,7] (CSH, 2.97 and 2.81 Å) and calcite[8] (2.45 Å) appeared even in the filler treated with the least amount of alkali, 1.25% CaO. Those prepared with more than 3% CaO showed some weak peaks of unknown significance around 4.85—4.91, 3.20 and 2.65 Å.

The results indicate that the M-1 fillers substantially

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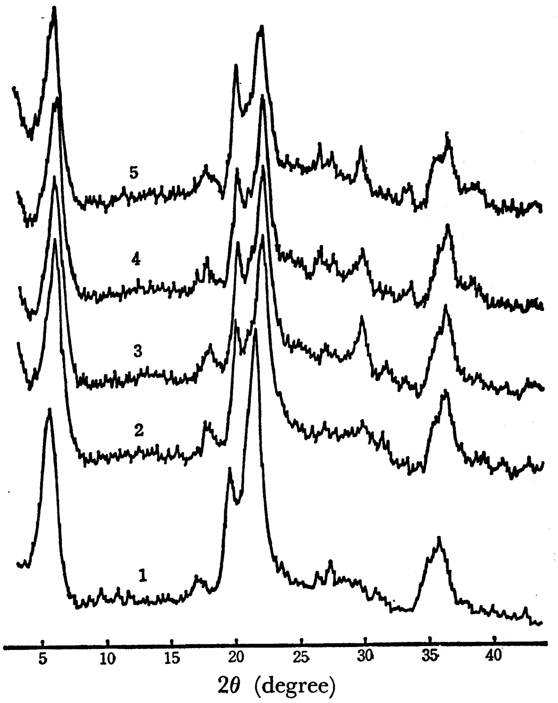


Fig. 1(a). X-Ray powder diagrams of M-1 series fillers in comparison with that of the original acid clay. (Cu$K\alpha$ radiation).
Curve 1: Matsune acid clay pulverized under 200 mesh and dried at 110 °C for 2 hr without lime treatment and calcination beforehand.
Curves 2—5: M-1 series fillers treated with hydrated lime (1.25, 3, 6 or 9% CaO, respectively), disintegrated by wet ball-milling for 18 hr and dried at 110 °C for 5 hr without calcination.

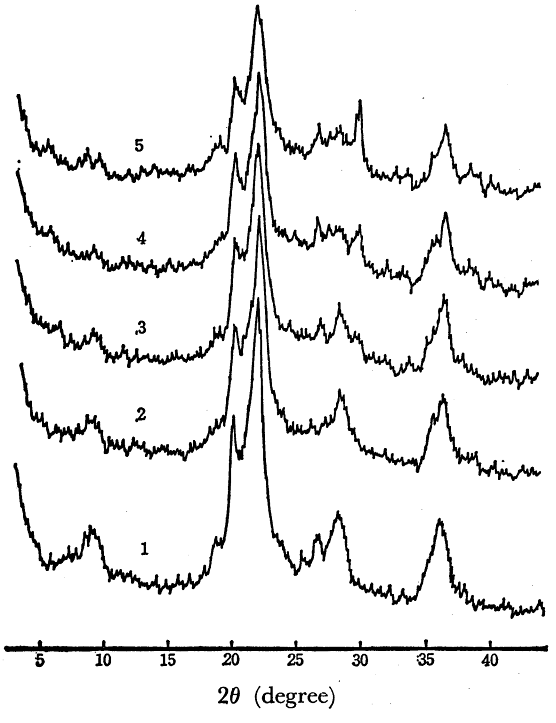


Fig. 1(b). X-Ray powder diagrams of M-2 series fillers. Curves 1—5 show the fillers prepared with or without hydrated lime (0, 1.25, 3, 6 or 9% CaO, respectively) followed by calcination (600 °C, 1.5 hr) and mechanical disintegration (wet ball-milling 18 hr).

retain the montmorillonite lattices with no significant structural changes though the conversion of the crystallite into Ca-montmorillonite, the consumption of the excess silica with alkali and the formation of small amounts of CSH, calcite and unknown crystalline materials were observed.

(ii) M-2 fillers: The basal reflection of montmorillonite almost disappeared. The remaining portion shifted towards lower spacings in the range 1.01—6.12 Å, in which the greatest shift occurred in the filler treated with 3% CaO (Fig. 1 (b) curves 1—5). A close relationship can be suggested with the reinforcing properties of the best **M** hard clay.

The most prominent reflection of α-cristobalite also decreased in proportion to the increase in the amount of alkali. New reflections analogous to those of the M-1 fillers appeared with relatively less intensity. They showed in sharpened mode as the reflections of the distinguished α-cristobalite and remaining montmorillonite.

Consequently, more structural changes occurred in the M-2 fillers than in the M-1 fillers. However, the minute crystallites still retained the montmorillonite lattices with no serious collapse though the capability

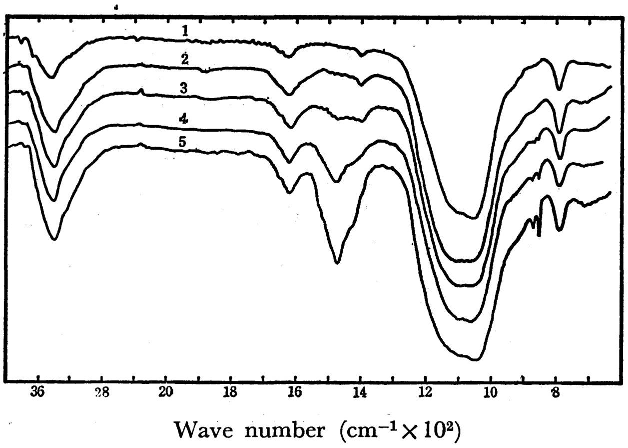


Fig. 2(a). Infrared spectra of M-1 series fillers in comparison with that of the original acid clay.
The respective curve corresponds to that of the same number shown in Fig. 1(a).

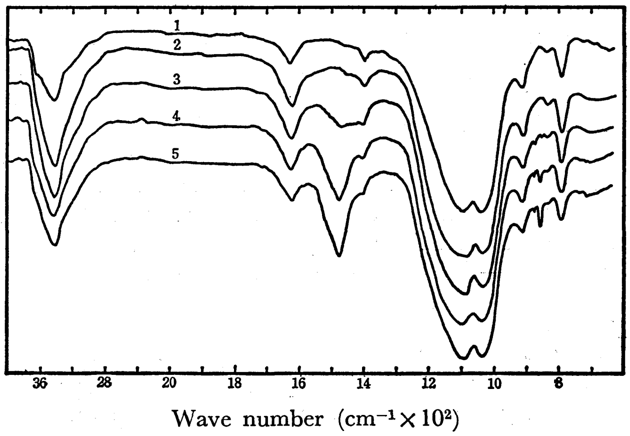


Fig. 2(b). Infrared spectra of M-2 series fillers. The respective curve corresponds to that of the same number shown in Fig. 1(b).

TABLE 1. INVESTIGATION OF STRUCTURE, MORPHOLOGY AND PHYSICOCHEMICAL PROPERTIES

	Methods	Apparatus	Conditions
Structure and morphology	X-ray diffraction	Rigaku Denki Geigerflex diffractometer	Nickel filtered Cu*K*α 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
	IR spectroscopy	JASCO Model DS-403G spectrophotometer	Through a KBr disk and Nujol mull in the regions 4000—200 and 4000—2800 cm^{-1}
	DTA and TG	Rigaku Denki Thermoflex differential thermogravimetric analyzer	From room temperature up to 1300 °C with a heating rate 10 °C/min
	Electron microscopy	JEOL JEM-6AS electron microscopy	Operated at 50 kV
Physicochemical properties	Hygroscopicity	Weighing bottle (10 ml), electric oven, desiccator and chemical balance	Expose a specimen (1 g) to the air for 24 hr, dry at 110 °C in an oven to constant weight and weigh the loss (wt%) before and after drying
	pH	pH meter with glass electrode	JIS K 6221-60 (1960); ASTM D 1512-57T (1957)
	DPG adsorption	Conical flask (200 ml) with stopper, centrifugal and titration apparatus	A modification[1] of the W. B. Wiegand and J. W. Snyder method, *I. E. C.*, **23**, 646 (1931). Adsorbate, 0.01 N DPG ethanol solution; indicator, 0.1% BPB ethanol solution
	Specific gravity	Pycnometer (10 ml), exhauster and chemical balance	ASTM D 153—39 (1939). Immersion liquid, kerosene (bp 70—100°C/2 mmHg, d_4^{30} 0.7811)
	Bulk density	Graduated, thick-walled test tube (20 ml) and rubber plate as a cushion	S. Kurabayashi, "Methods of Examination for Rubber and Relating Materials," ed. by S. Kunisawa, Soc. Rubber Ind. Japan (1963), p. 651.

of rehydration and rehydroxylation[9–11] disappeared almost completely as in the case of **N** hard clay (CaO less than 10%, calcination 600 °C, 1—1.5 hr; mechanical disintegration 18 hr).

(2) Infrared Spectra. Figures 2(a) and 2(b) illustrate the infrared spectra giving the difference of structural changes between the M-1 and M-2 fillers, respectively.

(i) M-1 Fillers: The diagnostic bands[12] of montmorillonite in the dried **M** varied with the treatment with alkali followed by mechanical disintegration and drying without calcination (Fig. 2(a) curves 1—5). As the amount of alkali increased, the bands at 3640 (νO–H, free), 3430 (νO–H, hydrogen bonded) and 1630 cm^{-1} (δO–H) in curve 1 first increased and then decreased as a result of the formation of Ca-montmorillonite and CSH (curves 2—5). The latter two bands slightly shifted towards lower frequencies at 3410 and 1620 cm^{-1}, respectively. The bands at 915 (δAl^{3+}–O–H)[13–15] and 853 cm^{-1} (δFe^{3+}–O–H)[13–15] decreased in proportion to the amount of alkali. The uptake of Ca^{2+} ion seems to take place in the outer edges of octahedrons of the montmorillonite. Of the bands characteristic of layer-lattice silicates in the regions 950—1250 (νSi–O) and 400—650 cm^{-1} (not shown), the band at 1100 cm^{-1} related to colloidal silica[16–18] became broad, the intensity considerably increasing, suggesting the progress of ion saturation.[19] However, the bands at 1035 and 472 cm^{-1} (δSi–O)[13–15] related to the skeletal vibrations of the tetrahedrons of montmorillonite and the band at 519 cm^{-1} (Si–O–Al^{VI})[13–15] remained unchanged.

New distinct bands at 1460—1475 and 855 cm^{-1} ascribable to CSH[20,21] increased in proportion to the decrease of the band at 794 cm^{-1} related to hydrated amorphous silica[16–18] with an increase in the amount of alkali. Only feeble bands at 1420, 876 and 715 cm^{-1} attributable to calcite,[22,23] which appeared in the fillers prepared with more than 3% CaO, hardly changed with the variation in the amount of alkali.

The results indicate that no significant alternation occurred in the montmorillonite lattices except for the formation of Ca-montmorillonite, CSH and calcite and the uptake of Ca^{2+} ion in the octahedrons.

(ii) M-2 Fillers: More changes appeared in the diagnostic bands of the montmorillonite than in the case of the M-1 fillers (Fig. 2(b) curves 1—5).

Irrespective of calcination (600 °C, 1.5 hr) for the fillers, the bands at 3430 and 1630 cm^{-1} increased in proportion to the amount of alkali. In view of the abrupt loss and noticeable shift in the basal reflections of calcined fillers, the increase can be attributed mainly to the water of crystallization of CSH. The bands were partially retained after calcination indicating rehydrated during the course of mechanical disintegration. The bands at 1035 and 472 cm^{-1} gradually shifted towards higher frequencies overlapping the adjacent bands at 1100 and 519 cm^{-1}, giving one stronger and broader band around 1060 and 485 cm^{-1}. Some irreversible contraction or condensation might take place in the montmorillonite lattices.

The band at 794 cm^{-1} decreased in intensity and became broader. This suggests the consumption of hydrated amorphous silica and the occurrence of partial polycondensation. The new bands ascribed to CSH and calcite appeared more distinctly than the

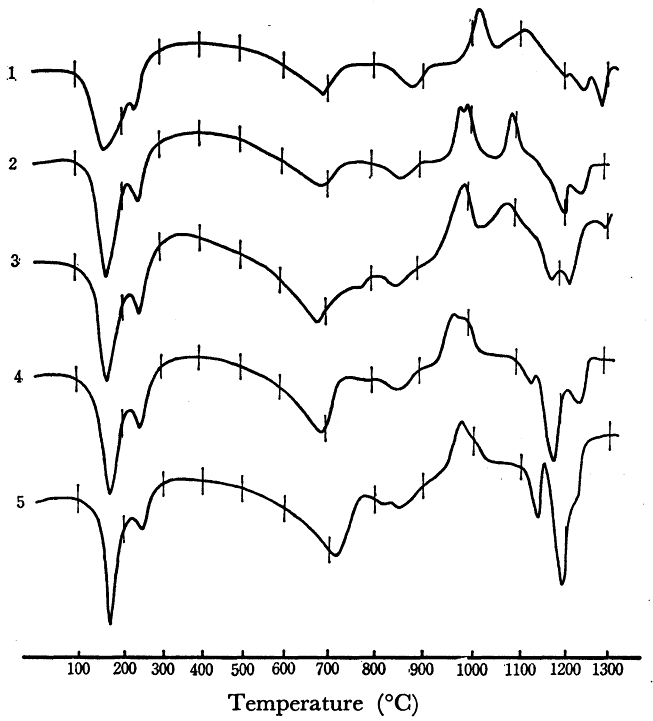


Fig. 3(a). DTA thermograms of M-1 series fillers in comparison with that of the original acid clay.
The respective curve corresponds to that of the same number shown in Fig. 1(a).

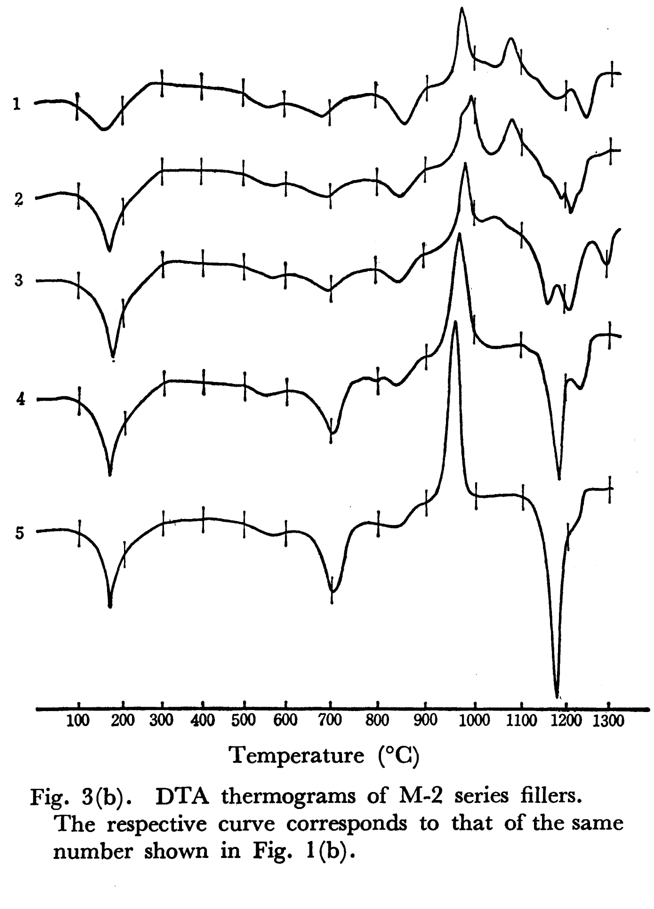


Fig. 3(b). DTA thermograms of M-2 series fillers.
The respective curve corresponds to that of the same number shown in Fig. 1(b).

corresponding bands of the M-1 fillers with an increase in the amount of alkali.

The fillers thus prepared still retained the minute crystallites of montmorillonite structure involving some irreversible contraction in the layer lattices. The consumption of α-cristobalite with alkali and partial polycondensation of the excess silica remained and the formation of new crystalline minerals such as CSH and calcite were observed in the matrix as well. The results agree with those of X-ray investigation.

(3) DTA Thermograms. Figures 3(a) and 3(b) show the DTA thermograms demonstrating the difference of structural changes between the M-1 and M-2 fillers, respectively.

(i) M-1 Fillers: The diagnostic peaks of montmorillonite[24—26] changed with the treatment as follows (Fig. 3(a) curves 1—5).

Endothermic Reactions: With an increase in the amount of alkali, the first two endotherms (152 °C, strong and broad; 225 °C, a medium shoulder) in the dried **M** (curve 1) became greater and gradually shifted towards higher temperatures; the filler treated with 9% CaO gave the endotherms at 173 and 243 °C (curve 5). The major endotherm in curve 1 is ascribable to dehydration[25,26] (100—300 °C) of the water adsorbed on the surfaces and among the interfaces of the minute crystallites of the montmorillonite and α-cristobalite, and the minor one to the water hydrated with the exchangeable cations interposed between the interlayers. With an increase in the amount of alkali, the major endotherm showed increase in the peak temperature, sharpness and symmetry of the profile (curves 2—5). This suggests that the dehydration can be explained in terms of the loss of the water of crystallization due to newly formed minerals CSH besides the adsorbed one.

The endotherm (685 °C, medium and broad) attributable to the dehydroxylation[25,26] (500—780 °C) of the normal montmorillonite and excess silica of the dried **M** showed a considerable rise in temperature around 9% CaO; the endotherm of the filler prepared with 1.25, 3, 6 or 9% CaO appeared at 683, 681, 685 or 709 °C, respectively. It was accompanied by a gradual increase in the area of profile. The results verify the formation of Ca-montmorillonite[25] and CSH[27] together with the appearance of the exotherm (around 970 °C) and endotherms (around 1130 and 1180 °C).

The endotherm (872 °C, medium and broad) due to the phase transition[25,26] (820—920 °C) of montmorillonite in the dried **M** gradually shifted towards lower temperatures, accompanied by a decrease in the area of profile; the filler prepared with 9% CaO gave the endotherm at 848 °C. An appreciable amount of Ca^{2+} ion should have been taken into the octahedrons of montmorillonite during the course of treatment.

The remaining endotherms at 1197 (a weak shoulder), 1237 (small and broad) and 1280 °C (medium and sharp) changed to 1132 (medium and sharp), 1185 (very strong and sharp) and 1222 °C (a medium shoulder), respectively.

The fusion point of the dried **M** (over 1300 °C) is lowered noticeably with the increase in the amount of alkali; the filler treated with 9% CaO melted at 1185 °C.

No endotherm ascribable to the dehydroxylation of calcium hydroxide (about 570 °C, strong),[27] which would take place during the course of mixing raw materials and subsequent mechanical disintegration, was found in both fillers. However, a weak one (around 772—812 °C) attributable to calcite[28] appeared in almost the same area for the fillers prepared with more than 3% CaO. This indicates that a nearly equal amount of calcite was produced in the fillers; the amount was estimated to be less than 3% from the area of endotherm. The formation resulted from the carbonation of liberated alkali $Ca(OH)_2$ during the course of preparation.

Exothermic Reactions: The exotherms due to β-quartz[24] or spinel[24] (1009 °C, medium and sharp) and β-cristobalite[24] (1102 °C, medium and broad) in the dried **M** showed splitting and sharpening, decreasing in the peak temperatures (979, 993 and 1085 °C) for the filler treated with the least amount of alkali, 1.25% CaO. With an increase in the amount of alkali, the exotherms gradually decreased in the temperatures and overlapped the adjacent peaks. The filler prepared with 9% CaO gave a medium and broad exotherm (972 °C) containing a weak shoulder (998 °C). The formation of some CSH gel in combination with alumina might be suggested.[27]

(ii) M-2 Fillers: The calcined **M** without the lime treatment showed a change in the diagnostic peaks of montmorillonite as follows (Fig. 3(b) curve 1).

Endothermic Reactions: The first two prominent endotherms (152 and 225 °C) in the dried **M** disappeared completely by calcination (600 °C, 1 hr). A medium and broad one (165 °C) appeared by subsequent mechanical disintegration (wet ball-milling 18 hr) and drying (110 °C, 5 hr). The first endotherm is ascribed to the dehydration of the water rehydrated during the course of the wet ball-milling. Disappearance of the minor one (225 °C) indicates that fixation[25] of the exchangeable cations interposed between the interlayers of the montmorillonite took place during the course of calcination.

The endotherm at 685 °C in the dried **M** diminished noticeably just after the calcination, and showed two peaks at 575 °C (small and broad) and 686°C (medium and broad) by the subsequent mechanical disintegration and drying. The endotherms are attributed to the dehydroxylation of the structural water rehydroxylated during the course of the wet ball-milling; the former (575 °C) corresponds to the disorder[10,25] of the montmorillonite lattices resulting from the calcination and mechanical disintegration, and the latter (686 °C) to the residual normal montmorillonite.

The endotherm (872 °C) due to the phase transition of montmorillonite in the dried **M** shifted towards a lower temperature (860 °C) with a slight increase in the area. During the course of calcination, some substitution[25] occurred in the octahedrons of the montmorillonite with the exchangeable cations originally interposed between the interlayers.

The remaining endotherms (1197, 1237 and 1280 °C) in the dried **M** moved to considerably lower temperatures (1130, 1193 and 1251 °C, respectively) with appreciable broadening in the calcined **M**.

Exothermic reactions: The exotherms due to β-quartz (1009 °C) and β-cristobalite (1102 °C) in the dried **M** also shifted towards lower temperatures (983 and 1080 °C, respectively), accompanied by appreciable sharpening in the calcined **M**. A pronounced crystallization would proceed by calcination without previous lime treatment. Additional treatment with hydrated lime caused noticeable changes in the DTA thermograms of the M-2 fillers (Fig. 3(b) curves 2—5).

Endothermic Reactions: As the amount of alkali increased, the first endotherm (165 °C) in the calcined **M** appeared around 180 °C. The endotherm gradually increased in the area and sharpness of profile. This can be attributed to the dehydration of the water of crystallization of CSH rehydrated during the course of wet ball-milling besides the readsorbed water distributed on the surfaces and among the interfaces of the minute crystallites.

The endotherm (575 °C) ascribed to the disorder of the montmorillonite lattices in the calcined **M** moved in succession towards a lower temperature (around 560 °C) with no change in the area of profile. However, the adjacent endotherm (686 °C) attributed to the dehydroxylation of the residual normal montmorillonite of the calcined **M** increased in the area, temperature and sharpness of the profile in proportion to the amount of alkali. This indicates a linear formation of CSH with an increase in the amount of alkali in accordance with the increase in the area and sharpness of the peaks observed around 180, 960 and 1180 °C. The filler prepared with 9% CaO gave the endotherm at 708 °C with more than three times area as compared with that of the calcined **M**.

An endotherm (795 °C) ascribable to calcite, easily observable by means of X-ray diffraction and IR spectroscopy, appeared only in the filler treated with 6% CaO.

The endotherm (860 °C) attributed to the phase transition of montmorillonite in the calcined **M** showed a gradual decrease in temperature (835 °C for 9% CaO) and the area (less than 1/3 for 9% CaO) of the profile. This suggests that the consumption of alumina proceeded in the octahedrons of the montmorillonite, resulting in the formation of CSH gel incorporated with alumina.

The endotherms appearing at 1193 and 1251 °C in the calcined **M** varied complicatedly with an increase in the amount of alkali. New peaks accompanied by an increase or a decrease in the area, shifting or overlapping adjacent peaks were observed.

Exothermic Reactions: The exotherm (983 °C) due to β-quartz in the calcined **M** showed a shoulder (975 °C) in the filler treated with the least amount of alkali, 1.25% CaO. The exotherm increased in the area and sharpness of profile, gradually decreased in the peak temperature in proportion to the amount of alkali and finally became one single peak. This suggests the formation of a considerable amount of CSH gel incorporated with alumina. The adjacent exotherm (1080 °C) ascribed to β-cristobalite in the calcined **M** decreased in the temperature and disappeared in the fillers treated with more than 6% CaO.

The greater the amount of alkali, the more advanced the formation of CSH (I, II and gel) and the greater the lowering of the fusion point; the one treated with 9% CaO melted at 1179 °C, about 120 °C lower than that of the dried **M**. Depression in the fusion point due to excess alkali over the optimum amount (CaO 3%) caused agglomeration, sintering or hardening of the minute crystallites of acid clay as in the case of polycondensation observed in the calcined **M** without previous lime treatment or in the fillers treated with alkali less than 3% followed by calcination. The calcined products became too hard to be sufficiently disintegrated. The reinforcing properties were reduced noticeably.

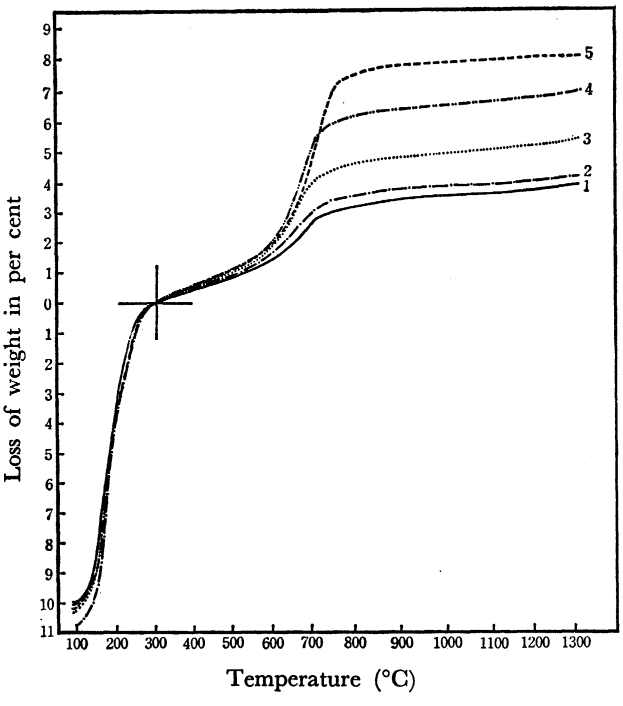


Fig. 4(a). TG thermograms of M-1 series fillers in comparison with that of the original acid clay.
The respective curve corresponds to that of the same number shown in Fig. 1(a).

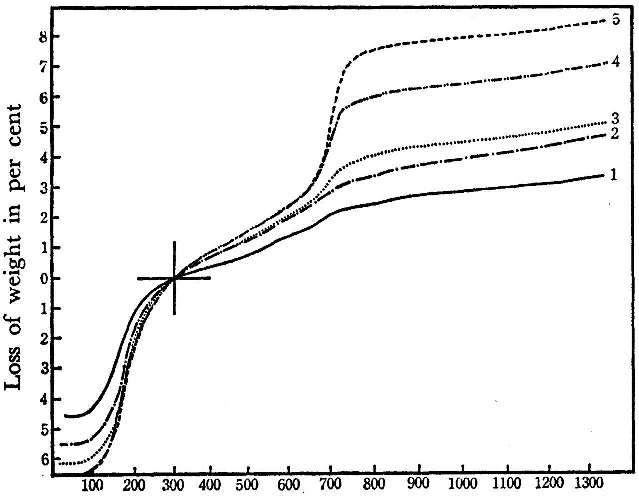


Fig. 4(b). TG thermograms of M-2 series fillers.
The respective curve corresponds to that of the same number shown in Fig. 1(b).

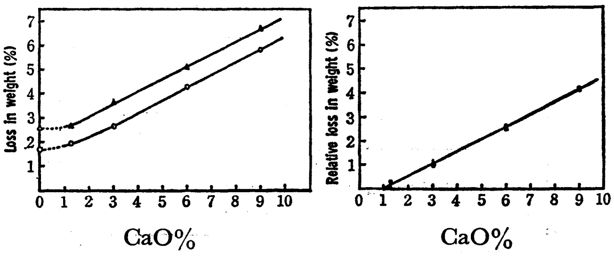


Fig. 4(c). A linear formation of CSH with an increase in the amount of CaO.
The relative loss in weight corresponds to the net weight loss related to the dehydroxylation of newly formed minerals.
△——△ M-1 series fillers; ○——○ M-2 series fillers.

(4) TG Thermograms. Figures 4(a) and 4(b) illustrate the TG thermograms of the M-1 and M-2 fillers, respectively. Four fractions, *viz.*, dehydration (up to 300 °C), oxidation (300—500 °C), dehydroxylation (500—780 °C) and phase transition (780—1300 °C), can be deduced with reference to the characteristic peaks of corresponding DTA thermograms.

Dehydration caused remarkable changes in weight; 7.8—11.9% and 4.3—6.2% for the M-1 and M-2 fillers, respectively.

Oxidation of adsorbed organic matter and/or the partial dehydration of newly formed minerals CSH (I, II and gel) resulted in a linear loss in weight; the loss varied within the ranges 0.76—1.11% and 0.71—1.57% for the M-1 and M-2 fillers, respectively.

A proportional increase in weight loss due to the dehydroxylation of the prepared fillers took place with an increase in the amount of alkali. The weight loss amounted to 2.59—6.66% and 1.67—5.77% for the M-1 and M-2 fillers, respectively.

The phase transition accompanied by or not by the fusion of specimen showed a linear loss in weight; it changed in the ranges of 0.90—1.39% and 0.74—1.77% for the M-1 and M-2 fillers, respectively.

The total loss in weight, consequently, increased with an increase in the amount of alkali; the M-1 fillers varied from 12.07 (CaO 0%) to 18.38% (CaO 9%) and the M-2 fillers from 7.56 (CaO 0%) to 14.22% (CaO 9%). Irrespective of calcination, the net loss in weight attributable to the dehydroxylation of the new minerals CSH was found to be accurately in proportion to an increase in the amount of alkali (Fig. 4(c)). The value can be estimated from TG thermogram by reducing the weight loss of a corresponding reference specimen, dried or calcined **M**, from that of a M-1 or M-2 filler, respectively. This indicates that the amounts of CSH produced in the fillers are proportional to those of the alkali. This is in line with the results obtained by X-ray diffraction, IR spectroscopy and DTA.

Determination of Physicochemical Properties. Changes in the physicochemical properties such as hygroscopicity, pH, DPG adsorption, specific gravity and bulk density are demonstrated in comparison with those of Dixie Clay, Silene EF and **M**, dried and calcined (Figs. 5(a)—

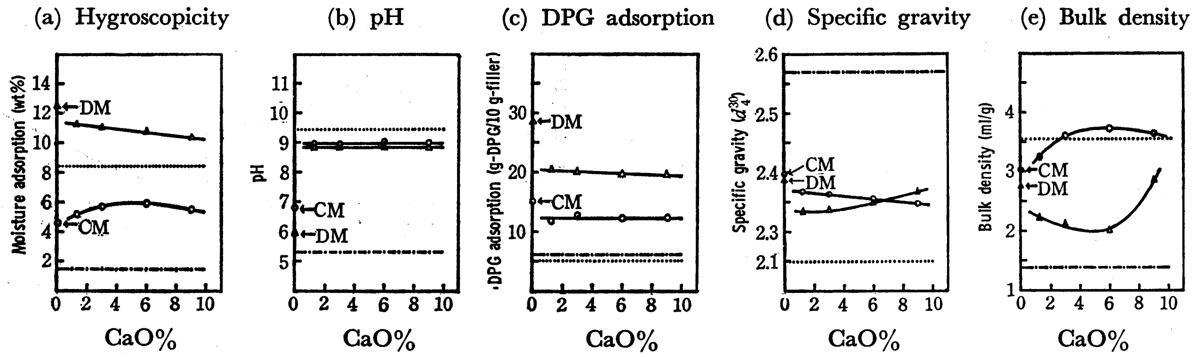


Fig. 5. Changes in the physicochemical properties of **M** hard clay with alkali (CaO 0—9%) and by thermal treatment (110 °C, 5 hr for M-1 series fillers; 600 °C, 1.5 hr for M-2 series fillers) in comparison with those of references, Dixie Clay, Silene EF and the original acid clay **M**, dried (110 °C, 2 hr) and calcined (600 °C, 1.5 hr).

Inscriptions are as follows: (a): Hygroscopicity (wt%), (b): pH, (c): DPG adsorption (g DPG/10^4 g filler), (d): Specific gravity (d_4^{30}), (e): Bulk density (ml/g), DM: Dried **M**, CM: Calcined **M**.

△——△ M-1 series fillers; ○——○ M-2 series fillers, —·—· Dixie Clay; ······ Silene EF.

(e)).

(1) Hygroscopicity: The hygroscopicity of the dried and calcined **M** without lime treatment were found to be 12.44 and 4.53%, respectively (Fig. 5 (a)). The former (12.44%) is much greater than the value of Dixie Clay (1.46%) or Silene EF (8.41%), and the latter (4.53%) is less than the mean value of the reference fillers.

By the lime treatment (CaO 1.25—9%) without subsequent calcination, the hygroscopicity of the M-1 fillers decreased in proportion to an increase in the amount of alkali. However, the value was still greater than that of Silene EF.

The hygroscopicity of the M-2 fillers decreased noticeably by the subsequent calcination (600 °C, 1.5 hr). The hygroscopicity was comparable to the mean value of the reference fillers, accompanied by a maximum around 6% CaO.

(2) pH: The pH of the dried and calcined **M** without previous lime treatment were found to be 5.95 and 6.77, respectively (Fig. 5 (b)). The values are smaller than the value of Silene EF (9.45) but close to that of Dixie Clay (5.30).

Treatment with hydrated lime and without subsequent clacination resulted in a noticeable increase in the pH of the M-1 fillers; a constant value as high as 8.84 was obtained.

Subsequent calcination gave rise to only a small increase (0.12) in the pH values of the M-2 fillers. They were comparable to the pH of Silene EF, deviating from that of Dixie Clay.

(3) DPG Adsorption: The DPG adsorption of **M** (dried 28.57 g DPG/10^4 g filler; calcined 15.03 g DPG/10^4 g filler) was found to be much greater than that of the reference fillers (Dixie Clay 6.05 g DPG/10^4 g filler; Silene EF 5.08 g DPG/10^4 g filler) (Fig. 5 (c)).

The DPG adsorption of the M-1 fillers decreased to a 70% value of the dried **M** by treatment with hydrated lime without subsequent calcination. Irrespective of the variation in the amount of alkali (CaO 1.25—9%), the value remained almost unchanged.

Subsequent calcination caused a further, constant diminution (7.73 g DPG/10^4 g filler) in the DPG adsorption of the M-2 fillers. A reduction to a 57% value of the dried **M**, twice as much as the value of Dixie Clay was observed.

(4) Specific Gravity: The specific gravity of the calcined **M** (2.3957) was found to be a little greater than that of the dried **M** (2.3891) (Fig. 5 (d)). The value of **M**, dried or calcined, is smaller than that of Dixie Clay (2.5684) but greater than that of Silene EF (2.0984).

Treatment with hydrated lime without subsequent calcination caused a noticeable decrease in the specific gravity of the M-1 fillers. The value, however, gradually increased with an increase in the amount of alkali.

Subsequent calcination resulted in a decrease in the specific gravity of the M-2 fillers in proportion to the amount of alkali. Consequently an intersection with the former plots appeared around 7% CaO.

The variation of the specific gravity of the M-1 and M-2 fillers with the amount of alkali remained in the ranges 0.0331 and 0.0203, respectively.

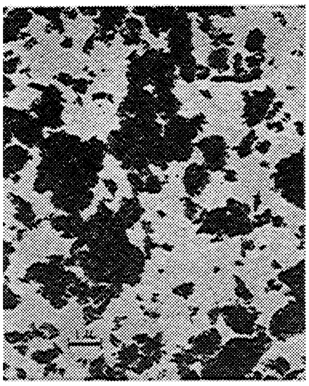
(5) Bulk Density: The bulk density of dried and calcined **M** was found to be 3.02 and 2.75 ml/g, respectively (Fig. 5(e)). The latter (2.75 cc/g) is comparable to the mean value of Dixie Clay (1.38 ml/g) and Silene EF (4.05 ml/g)

Treatment with hydrated lime less than 6% CaO without subsequent calcination caused a gradual decrease in the bulk density of the M-1 fillers. More alkali, however, gave rise to a rapid increase. Consequently a minimum value of the bulk density appeared around 4—6% CaO.

Subsequent calcination afforded a further increase in the bulk density of the M-2 fillers. A maximum exceeding the value of Silene EF was obtained with 5—7% CaO.

The results indicate that not only reduction in the hygroscopicity, DPG adsorption and specific gravity of the original acid clay **M**, but also increase in the pH and bulk density of the fillers can be attained by treatment with hydrated lime (CaO 1.25—9%) followed by calcination (600 °C, 1.5 hr) as compared with a single treatment with alkali or by calcination alone.

Morphological Study by Electron Microscopy and SAD



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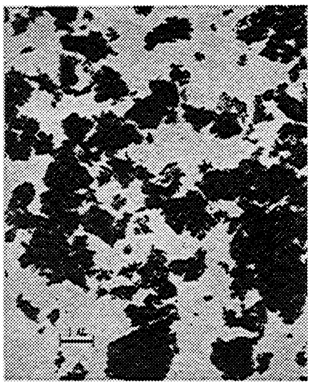

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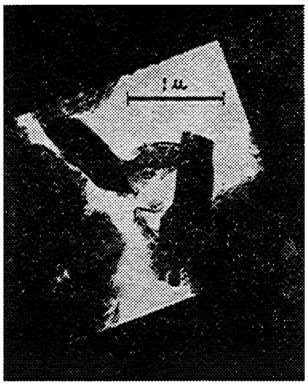

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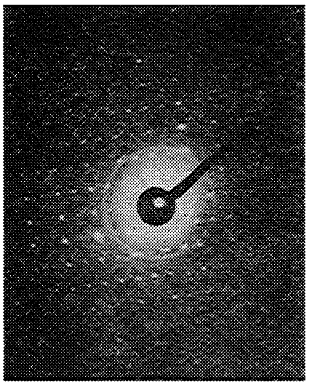

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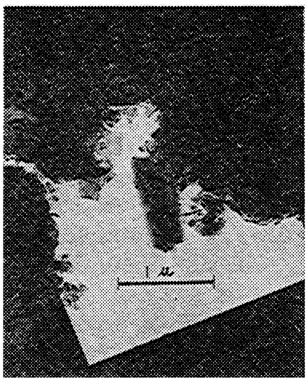

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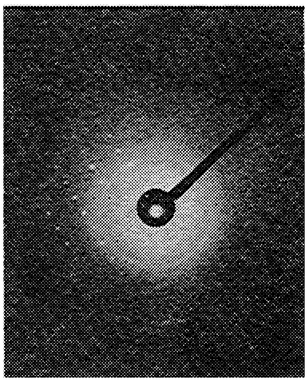

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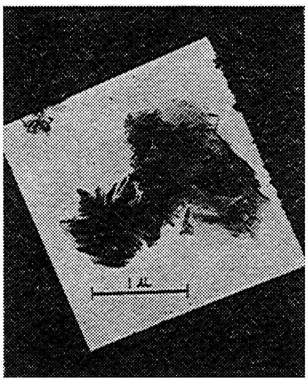

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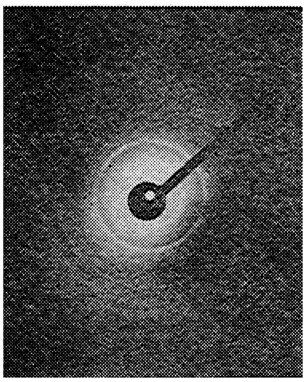

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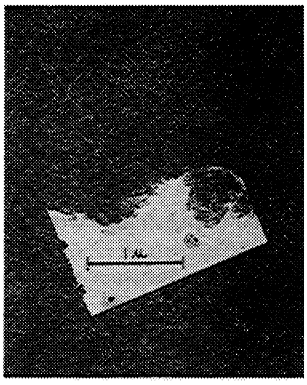

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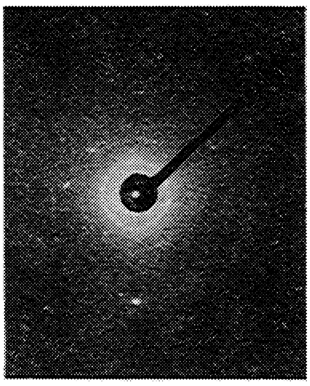

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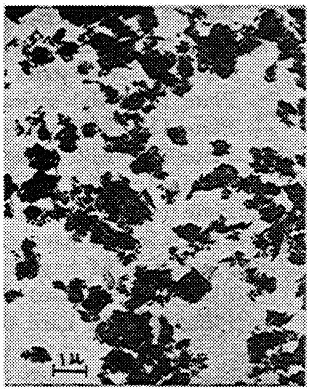

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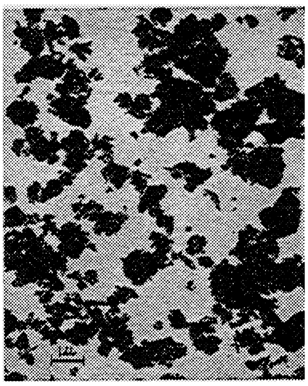

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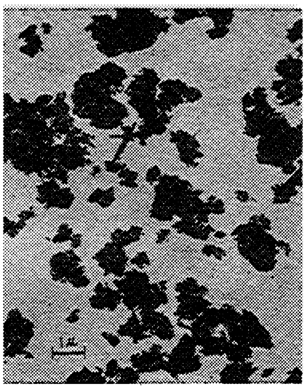

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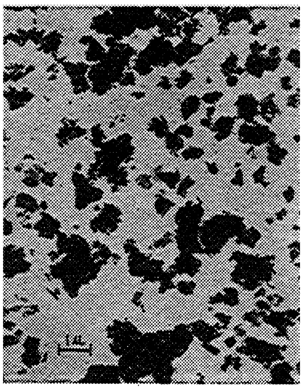

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Fig. 6. Electron micrographs and SAD diagrams of **M** hard clay with magnifications of 9000 and 26000, respectively in comparison with those of **N** hard clay.

Plate 1: **M** hard clay (CaO 6%; calcination 600 °C, 1 hr; wet ball-milling 18 hr).
Plate 2: **N** hard clay (CaO 6%; calcination 600 °C, 1 hr; wet ball-milling 18 hr).
Plate 3A: Well crystallized CSH in **M** hard clay (CaO 6%; calcination 600 °C, 1 hr; wet ball-milling 18 hr).
Plate 3B: The SAD diagram of the new mineral in Plate 3A.
Plate 4A: Thin, platey crystal of CSH in **M** hard clay (CaO 3%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 4B: The SAD diagram of the new mineral in Plate 4A.
Plate 5A: Poorly crystallized aggregate in **N** hard clay (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 5B: The SAD diagram of the aggregate in Plate 5A.
Plate 6A: Cluster of globular-shaped CSH in **M** hard clay (CaO 3%; wet ball-milling 18 hr; drying 110 °C, 5 hr).
Plate 6B: The SAD diagram of the cluster in Plate 6A.
Plate 7: M-1 series filler (a) (CaO 1.25%; wet ball-milling 18 hr; drying 110 °C, 5 hr).
Plate 8: M-1 series filler (b) (CaO 3%; wet ball-milling 18 hr; drying 110 °C, 5 hr).
Plate 9: M-1 series filler (c) (CaO 6%; wet ball-milling 18 hr; drying 110 °C, 5 hr).
Plate 10: M-1 series filler (d) (CaO 9%; wet ball-milling 18 hr; drying 110 °C, 5 hr).
Plate 11: M-2 series filler (a) (CaO 1.25%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 12: M-2 series filler (b) (CaO 3%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 13: M-2 series filler (c) (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 14: M-2 series filler (d) (CaO 9%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 15: **M** hard clay (1) (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 6 hr).
Plate 16: **M** hard clay (2) (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 12 hr).
Plate 17: **M** hard clay (3) (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr).
Plate 18: **M** hard clay (4) (CaO 6%; calcination 600 °C, 1.5 hr; wet ball-milling 24 hr).

Technique. **M** hard clay gave a greater amount and smaller size of particle than **N** hard clay under the same conditions of preparation (Fig. 6, Plate 1 *cf.* Plate 2). This can be attributed mainly to the difference of mineralogical constituents between the original acid clays, **M** and **N**, *viz.*, the amounts of normal and abnormal montmorillonites as well as excess silica α-cristobalite.

The deviation in the optimum amount of hydrated lime in the best reinforcing fillers (CaO 3% for **M**, 6% for **N**; calcination 600 °C, 1.5 hr; wet ball-milling 18 hr) can be interpreted in the same way. The SAD technique applied to the best reinforcing fillers and others revealed that a distinct diffraction pattern of CSH appeared in **M** hard clay but only a feeble one in **N** hard clay besides the diagnostic reflections of montmorillonite (Plates 3-A, 3-B, 4-A and 4-B *cf.* 5-A and 5-B), and that subsequent calcination affected the formation of CSH noticeably (Plates 4-A and 4-B *cf.* Plates 6-A and 6-B).

The fact that the greater part of hydrated lime added to **N** is combined with the montmorillonite lattices is interpreted as follows: (i) **N** consists of abnormal montmorillonite in a greater amount than normal montmorillonite,[1] (ii) the former reacts with alkali more easily than the latter, (iii) the amount of excess silica involved in **N** (13%) is much less than in **M** (34%),[1] (iv) α-cristobalite contained in the interior of montmorillonite lamellae reacts with alkali with more difficulty than the one distributed on the surface of crystallite or in an isolated state.

The less the content of excess silica involved in the original acid clay, the less the formation of CSH in the fillers prepared with the same amount of alkali. However, the formation of CAH and calcite increased with an increase in the amount of alkali. This agrees with the results obtained by X-ray diffraction and IR spectroscopy.

The indispensability of thermal treatment at an appropriate temperature for the preparation was proved by comparing the morphology of the M-1 and M-2 fillers (Plates 7—10 *cf.* Plates 11—14). After mechanical disintegration in wet state for 18 hr, the particle size and its distribution range of the M-1 fillers were found to be even smaller than those of the corresponding M-2 fillers. During the course of drying, however, the active silanol groups, originally contained and mechanochemically[29,30] generated in the wet ball-milling, and alkali liberated in the matrix cause the recombination of minute crystallites of the fillers, resulting in the formation of much greater and harder agglomerates. Subsequent pulverization with an atomizer to minimize the agglomerates is so difficult that the reinforcing effect of the M-1 fillers on SBR-1502 compounds decreased noticeably.[2]

In the case of the M-2 fillers, calcination (600 °C, 1.5 hr) after lime treatment gives rise to adequate dehydroxylation as well as dehydration of the montmorillonite, CSH and excess silica remaining. This process helps to facilitate the pulverization of the final products and also has the effect of inhibiting polycondensation of montmorillonite and α-cristobalite due to an even formation of the CSH distributed on the interlayer surfaces and the interfaces of the minute crystallites. Thus the great surface activity inducing agglomeration during the course of drying and the great adsorption encountered in compounding can be restrained properly.

The reduction of the particle size and its distribution range of the same-series fillers was found to be proportional to the time of mechanical disintegration up to 18 hr (Plates 15—18).

Conclusion

In spite of the similarity in the constitutional units, fineness and functional groups of montmorillonite and kaolinite, acid clays, hitherto, could not be utilized as a material for reinforcing fillers due to structural factors[31,32] such as substitutions in the tetrahedral and/or octahedral sheet, nonconformity in the layers and lattice defects of montmorillonite which cause too great adsorption, cation exchange, swelling and catalytic activity.

It has been found that treatment with hydrated lime followed by calcination and mechanical disintegration can suppress the great surface activity of acid clay and maintain the fineness and available functional groups of the crystallites properly, turning acid clays into a reinforcing filler.

The reinforcing effect on SBR-1502 compounds was found to be in line with the reduction in both the particle size and its distribution range. The average particle size and its distribution are closely related to the mineralogical constituents of the original acid clays, **K**, **M** and **N**, as well as the conditions of preparation as in the case of the contents of remaining functional groups and newly formed minerals, CSH, CAH and calcite.[1-3] The optimum conditions for the preparation were found to be as follows: Raw materials consist of normal and/or abnormal montmorillonite involving excess silica α-cristobalite as principal constituents. Treatment with hydrated lime (CaO 3% for **M**, 6% for **N**) followed by calcination (600 °C, 1.5 hr) and mechanical disintegration (wet ball-milling 18 hr).

The precise mechanism of the reinforcing effects caused by the prepared fillers has not been clarified. However, it is certain that surface energy, especially the interaction between the hydroxyl radicals distributed on the outer surfaces of filler particles and compounded elastomer molecules play the most important role.[33,34]

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