Preparation of Reinforcing Fillers from Japanese Acid Clays with Lime and by Calcination. III. Elucidation of the Reinforcing Effects Based on the Investigation of Changes in the Structure, Physicochemical Properties and Morphology of N Hard Clay

Hideki Rai and Junkichi Yamada*
The Institute of Industrial Science, The University of Tokyo, Minato-ku, Tokyo 106

(Received November 5, 1974)

In order to elucidate the reinforcing effects of the fillers prepared from Japanese acid clay with hydrated lime and by calcination and mechanical disintegration, **N** hard clay (CaO 3—60%; calcination 400—800 °C, 1—1.5 hr; wet ball-milling 18 hr) derived from Nakajo acid clay (**N**) were investigated on the structure, physicochemical properties and morphology in comparison with those of **N**, Dixie Clay and Silene EF. X-Ray diffraction, infrared spectroscopy and electron micrography were applied to the examination of the structural and morphological features. The physicochemical properties were determined on the surface properties such as hygroscopicity, pH and DPG adsorption together with the specific gravity and bulk density. The following results were obtained: (1) Treatment under the optimum conditions (CaO 6%, calcination 600 °C, 1.5 hr; wet milling 18 hr) caused a favorable change in the structure of the prepared filler, resulting in controlling the surface properties, reduction in the particle size and its distribution, a decrease in the specific gravity and an increase in the bulk density. (2) Deviation from the conditions, *e.g.*, calcination at 400 °C for 1.5 hr remained too much residual adsorptivity to improve the great surface activity of **N**, whereas treatment at 800 °C for 1—1.5 hr afforded sintering, collapse and/or fusion yielding too hard aggregates to be disintegrated as well as a serious breakdown or complete loss in the effective functional groups involved.

Previously we reported the studies of the availability of some Japanese acid clays such as Nakajo (**N**), Matsune (**M**) and Kuramitsu (**K**) origins for the preparation of a reinforcing filler of elastomers,[1] the optimum conditions for producing good hard clays from **M** and **N**, and their reinforcing properties.[2]

Further investigations were carried out in order to elucidate the reinforcing effects in connection with the characteristics of structure, morphology and physicochemical properties of the fillers prepared. The **N** hard clay derived from **N** were investigated on the structure and morphology by means of X-ray diffraction, infrared spectroscopy and electron micrography. The physicochemical properties such as hygroscopicity, pH, DPG adsorption, specific gravity and bulk density were determined as described before. The features of the structure, morphology and physicochemical properties were compared with those of reference fillers, Dixie Clay, Silene EF, and dried or calcined **N** without lime treatment beforehand. Valuable information elucidating the characteristics of **N** hard clay with relation to the reinforcement was obtained.

Experimental

Materials. The **N** hard clay prepared under the various conditions of treatment (CaO 3—60%; calcination 400—800 °C, 1—1.5 hr; wet ball-milling 18 hr) described in the preceding paper[2] were put to use.

Dixie Clay, Silene EF and Nakajo acid clay **N**, dried in air (24 hr), in oven (110 °C, 2 hr) or calcined (400—800 °C, 1 hr) without the lime treatment and mechanical disintegration, were used as references.

Determination of Structure, Morphology and Physicochemical Properties. The same apparatus and conditions of measurement as mentioned before[1] were followed in the investigation of changes in the structure, morphology and physicochemical properties of the fillers prepared.

Results and Discussion

Treatment of the original acid clay with hydrated lime follwed by calcination and mechanical disintegration caused noticeable changes in the structure, physicochemical properties and morphology of the fillers obtained.

(1) Structural Changes. *(a) X-Ray Diffraction Patterns*: Figures 1(a)—(c) illustrate the X-ray powder diffraction patterns of **N** hard clay showing the structural changes in comparison with those of the dried or calcined **N** without the lime treatment beforehand.

It is apparent that all the hydrated lime (4.90 and 2.63 Å)[3] added to **N** has disappeared as a result of the reaction during the treatment.

An increase in the amount of alkali and the temperature of calcination for the prepared fillers resulted in some basal shift of an irreversible contraction along the c-axis of montmorillonite lattices as well as the diminution or even disappearance of the prominent basal reflection (15.77 Å (001))[4] of the montmorillonites, normal and abnormal,[1] in the air-dried **N**.

Coincidently an almost proportional decrease in the intensity of excess silica α-cristobalite (4.04 Å (101))[5] occurred in the fillers as the amount of alkali increased.

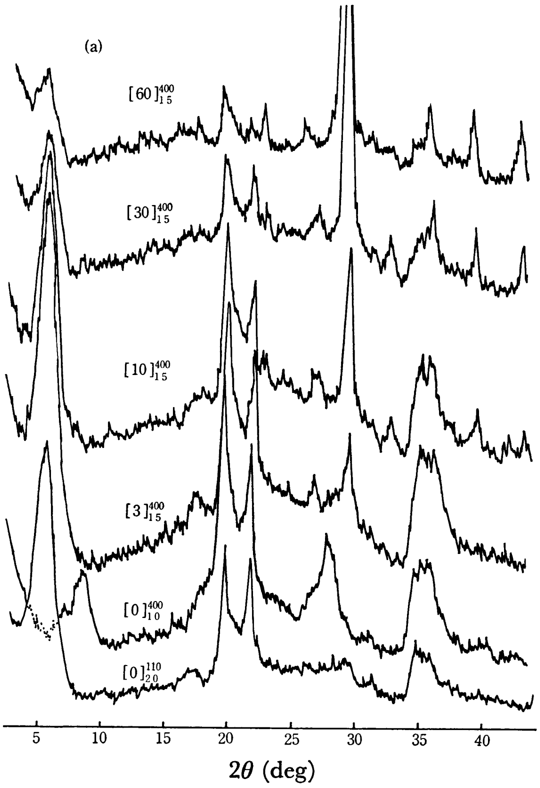
New reflections also appeared approximately in proportion to an increase in the amount of alkali. They were ascribed to calcium silicate hydrates of tobermolite group (CSH I, II and G; 2.90—3.08, 2.78—2.85 and 1.80—1.85 Å)[6,7] and calcite (3.86, 3.04, 2.50, 2.28 and 2.09 Å).[8] The former was generated by the reaction of hydrated lime with the excess silica

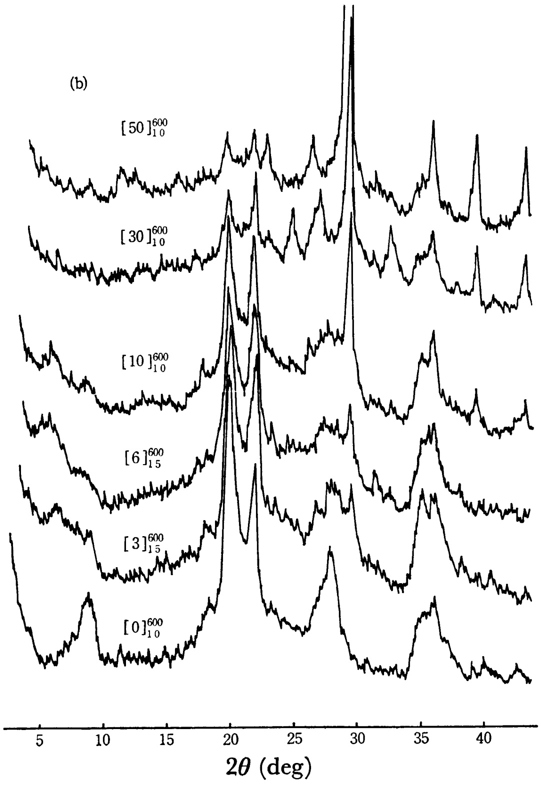
---

* Present address: AA Chemical Co., Ltd., Shibakoen, Minato-ku, Tokyo 105.

covering the external and internal surfaces of the montmorillonite crystallites or existing in an isolated state, and the latter by the carbonation of the alkali liberated during the courses of mixing raw materials followed by filtration, drying, calcination and mechanical disintegration.

(i) Calcination at 400 °C for 1—1.5 hr (Fig. 1 (a)). The basal reflection (15.77 Å) of the air-dried **N** shifted towards 10.04 Å and decreased the intensity as much as 72.1% by the calcination at 400 °C for 1 hr without the lime treatment and mechanical disintegration.





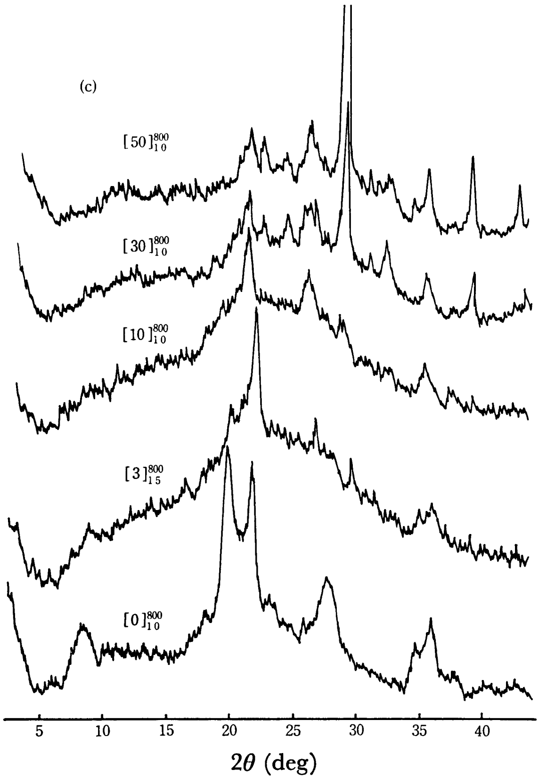


Fig. 1. X-ray diffraction patterns of **N** hard clay (CaO 3—60%; calcination 400—800 °C, 1—1.5 hr; mechanical disintegration 18 hr) in comparison with those of Nakajo acid clay **N**, dried (110 °C, 2 hr) or calcined (400—800 °C, 1 hr) without further treatment. Inscriptions are as follows. (a): CaO 3—60%; calcination 400 °C, 1—1.5 hr; wet milling 18 hr. (b) CaO 3—50%; calcination 600 °C, 1—1.5 hr; wet milling 18 hr. (c): CaO 3—50%; calcination 800 °C, 1—1.5hr; wet milling 18 hr.

* Number in brackets indicates the amount of alkali used, and the superscript and subscript numbers of the brackets denote the temperature and time of calcination, respectively.

Irrespective of the change in the amount of alkali (CaO 3—60%), the fillers prepared without the calcination showed a nearly constant shift (about 2 Å) in the basal reflections as a result of the formation of Ca-montmorillonite. The intensity of the basal reflection first increased with less than 10% CaO and then decreased with more than 30% CaO. The increase in the intensity of the basal reflection is considered to be based on the saturation of the Ca^{2+} ion interposed between the interlayers of the montmorillonites, and the decrease on the erosion initiated from the edges and outer surfaces of the crystallites with the hydrated lime. These reactions should be accelerated mechanochemically during the course of mixing raw materials, especially by the wet ball-milling.

The subsequent calcination at 400 °C for 1.5 hr and by the wet milling for 18 hr gave a considerable diminution (24.5, 39.6, 72.3 and 83.7% for 3, 10, 30 and 60%

CaO, respectively) in the basal reflection as well as a slight shift (1.97, 1.75 and 1.53 Å for 3, 10—30 and 60% CaO, respectively).

In view of the changes in the intensities and shifts of the basal reflections of the calcined **N** and the fillers prepared without such a calcination as mentioned above, the decrease in the basal shift of the fillers with an increase in the amount of alkali suggests that the formation of CSH as well as the erosion would proceed on the lamellae surfaces of the montmorillonite crystallites. The remained intensity (75.5—16.3% for 3—60% CaO) and the relatively small shift (less than 2 Å) of the basal reflection indicate that noticeable capabilities of rehydration and rehydroxylation[9-11] were still reserved in the fillers obtained. Consequently the inherent, great surface activity of the original acid clay **N** was restrained insufficiently by this procedure, which would be discussed in detail in connection with the physicochemical properties later.

(ii) Calcination at 600 °C for 1—1.5 hr (Fig. 1 (b)). The calcined **N** (600 °C, 1 hr) prepared without the lime treatment and mechanical disintegration gave an irreversible contraction (5.90 Å) in the montmorillonite lattices as well as a noticeable diminution (81.2%) in the intensity of the basal reflection, which were greater than those of the calcined **N** (400 °C, 1 hr) described above. Nevertheless, exhaustive dehydroxylation or the formation of anhydrous modification[12,13] could not be observed in the crystallites.

The treatment with hydrated lime (3—50% CaO) followed by calcination at 600 °C for 1 or 1.5 hr and the same mechanical disintegration as above afforded a further shift (2.59, 1.75 and 1.05 Å for 3, 6 and 10% CaO, respectively) and a greater diminution (91.2, 89.9 and 93.1% for 3, 6 and 10% CaO, respectively) than the corresponding values of the foregoing fillers (CaO 3—60%; 400 °C, 1.5 hr; wet milling 18 hr) or even resulted in the disappearance (for more than 30% CaO) of the basal reflection in the prepared fillers.

The intensity of α-cristobalite also decreased with an increase in the amount of alkali.

The reactions including thermal dehydration and dehydroxylation, fixation and substitution with Ca^{2+} ion, erosion by free alkali and the formation of CSH proceeded so extensively in the crystallites that the capability of rehydration and rehydroxylation during the wet milling decreased noticeably. However, the minute crystallites still persisted the montmorillonite lattices, even though they were eroded considerably.

The results obtained indicate that as the calcining temperature increased, the irreversible contraction along the c-axis of the montmorillonite lattices increased especially with a less amount of alkali, and that an increase in the amount of alkali resulted in the moderation of the thermal contraction. The moderation should be attributed mainly to the formation of CSH on the lamellae surfaces of the minute crystallites.

The treatment with alkali more than 10% CaO followed by calcination at temperatures higher than 600 °C for more than 1 hr gave the formation of calcium aluminate hydrates (CAH) (7.7 and 5.6 Å ascribable to C_4AH_{13})[6,7,14] and the appearance of some peaks of unknown significance (5.6, 4.94 and 3.36 Å for 50% CaO and 5.11, 3.57 and 3.28 Å for 30% CaO).

(iii) Calcination at 800 °C for 1—1.5 hr (Fig. 1 (c)). The calcined **N** (800 °C, 1 hr) prepared without the lime treatment and mechanical disintegration afforded an irreversible contraction (5.73 Å) of the montmorillonite lattices and a noticeable diminution (83.02%) in the intensity of the basal reflection. The basal spacing (10.04 Å) is slightly greater than those of the calcined **N** (600 °C, 1 hr; 9.87 Å) described above as well as the dehydrated layer (9.5 Å)[4] of montmorillonite, indicating the occurrence of an appreciable expansion of the crystallites.

The most serious structural changes appeared in the fillers treated with hydrated lime (3—50% CaO) followed by calcination at 800 °C for 1 or 1.5 hr and mechanical disintegration for 18 hr; all reflections of the montmorillonites disappeared completely in almost of the fillers obtained. Especially those prepared with less than 10% CaO accompanied very diffused and broadened reflections due to amorphous phases, indicating the appearance of sintering or partial fusion of the minute crystallites besides the collapse in the montmorillonite lattices. The less the amount of alkali and the higher the temperature of calcination, the greater the effect on the structural changes in the fillers prepared. In view of the appearance of relatively less intensities of CSH and calcite than in the cases of the lower-temperature calcination described above, a greater part of the alkali should be incorporated into the montmorillonite lattices.

(b) Infrared Spectra: Figures 2 (a)—(c) give the infrared spectra of the prepared fillers in comparison with those of **N**, dried or calcined without the lime treatment. The diagnostic bands[15] of montmorillonite in **N** varied with the treatment with hydrated lime followed by calcination and mechanical disintegration, and those of the new minerals appeared.

(i) Calcination at 400 °C for 1.5 hr (Fig. 2 (a)). The band at 3650 cm^{-1} (νO–H, free) observable in the dried **N** decreased with an increase in the amount of alkali added to the fillers prepared (CaO less than 10%; calcination 400 °C, 1.5 hr; wet milling 18hr), and disappeared with more than 30% CaO as a result of the formation of Ca-montmorillonite and CSH as confirmed by X-ray diffraction. Whereas the calcination without the lime treatment and mechanical disintegration remained the band up to 600 °C, although the intensity decreased with an increase in the temperature of calcination.

The bands at 914 (δAl^{3+}–O–H)[16] and 836 cm^{-1} (δFe^{3+}–O–H)[17] completely disappeared in the fillers prepared with more than 30% CaO. Whereas the calcined **N** (400 °C, 1 hr) which had excluded the lime treatment still reserved the former band slightly. The both bands were barely lost by the calcination over 600 °C for 1 hr.

Among the bands of layer silicates in the region 900—1200 cm^{-1} (νSi–O), the band at 1081 cm^{-1} related to colloidal silica[18-20] and ion saturation[21] as well as the band at 796 cm^{-1} (δSi–O) related to hydrated amorphous silica[18-20] gradually decreased the

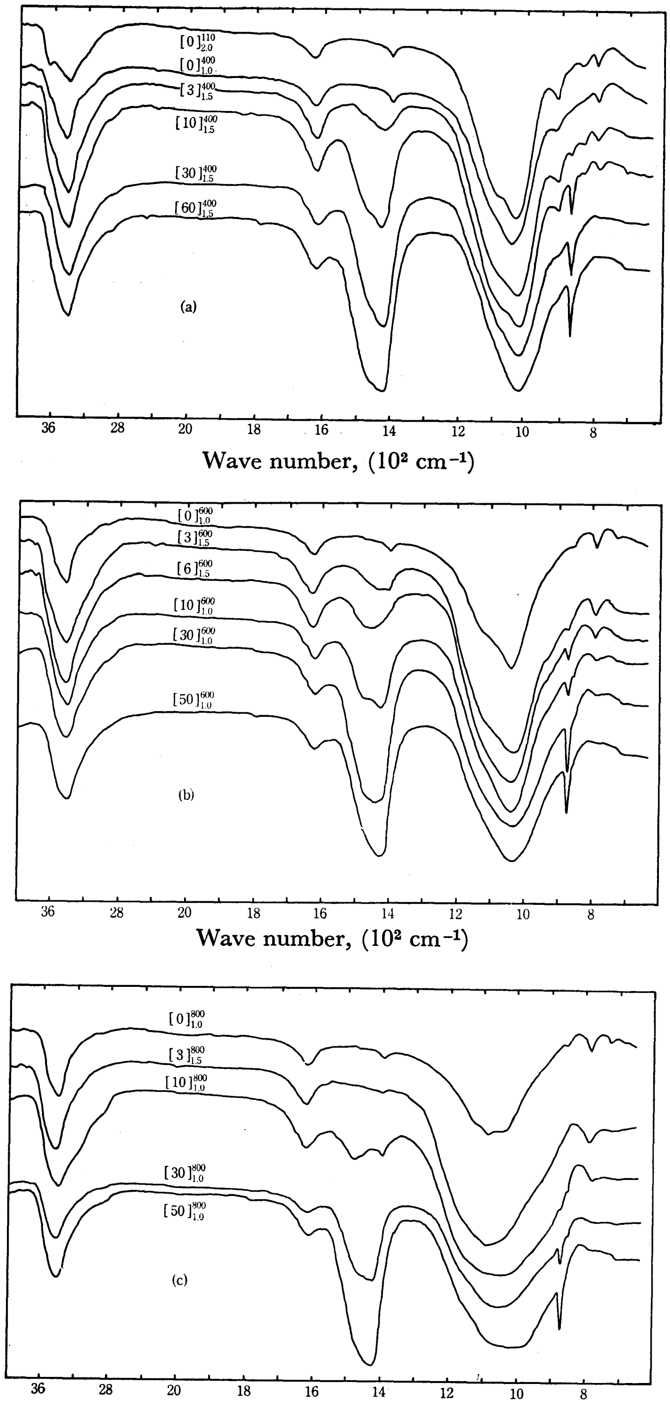


Fig. 2. Infrared spectra of **N** hard clay (CaO 3—60%; calcination 400—800 °C, 1—1.5 hr; mechanical disintegration 18 hr) in comparison with those of Nakajo acid clay **N**, dried (110 °C, 2 hr) or calcined (400—800 °C, 1 hr). The same inscriptions as in Fig. 1 are applied.

intensities as the amount of alkali increased. The latter was barely lost with more than 60% CaO in accordance with the consumption of the excess silica α-cristobalite observable in the foregoing X-ray diffraction. The abnormally great deviation in the amount of alkali required for the complete reaction with the excess silica (13%)[1] involved suggests that considerable amounts of hydrated lime were consumed by carbonation, fixation or trapping in the interior of the crystallites, substitution and some other reactions with Ca^{2+} ion in the tetrahedrons and octahedrons of the montmorillonites. The formation of calcite, CSH, CAH and some other calcium salts resulted consequently. The band at 1035 cm^{-1} related to the skeletal vibrations of the tetrahedrons of montmorillonite slightly shifted towards a lower frequency at 1025 cm^{-1} with appreciable broadening[21] with more than 30% CaO, verifying the above suggestion.

The bands ascribable to the newly formed minerals, CSH (1480 and 855 cm^{-1})[22,23] and calcite (2520, 1790, 1430, 876, and 715 cm^{-1}),[24,25] in the fillers increased with an increase in the amount of alkali.

The bands at 3410 and 1630 cm^{-1} in the calcined **N** decreased in proportion to an increase in the temperature of calcination. They are related to the waters adsorbed on the surfaces and among the interfaces of the minute crystallites and those hydrated with the exchangeable cations interposed between the interlayers of the montmorillonites. Irrespective of the calcination at 400 °C for 1.5 hr, they increased the intensities noticeably in the fillers as the amount of alkali increased. This can be explained in terms of the residual adsorptivity of the montmorillonites inducing considerable rehydration and rehydroxylation. The crystal water of CSH, remained after the calcination and rehydrated during the course of the wet milling for 18 hr, also contributed additionally.

(ii) Calcination at 600 °C for 1—1.5 hr (Fig. 2 (b)). The band at 3650 cm^{-1} was lost by degrees in the fillers treated with more than 10% CaO followed by the calcination (600 °C, 1—1.5 hr) and the same disintegration.

The bands at 914 and 836 cm^{-1} disappeared completely in those prepared with more than 3% CaO or even by the calcination (600 °C, 1 hr) alone without the lime treatment in advance.

The bands at 1081 and 796 cm^{-1} decreased more slowly with an increase in the amount of alkali than in those of the fillers calcined at 400 °C for 1.5 hr, and barely disappeared with more than 50% CaO. Diminution in the reactivity of the excess silica with alkali can be attributed mainly to more favorable polycondensation and/or the crystallization of the amorphous silica and α-cristobalite at 600 °C rather than 400 °C on the basis of a noticeable increase in the sharpness of the corresponding peaks in the X-ray diffraction patterns (Fig. 1 (a) *cf.* (b)). The phenomena of crystallization of silica gels, analogous to the natural aging of gels to hyalite and so on, are extensively studied by X-ray diffraction and other methods,[26,27] and are well known to be accelerated by thermal treatment.[28,29]

A new phase ascribable to pyrophillite dehydroxylate (864, 795, and 730 cm^{-1})[9] appeared in the fillers treated with less than 3% CaO, suggesting the occurrence of appreciable transformation as well as exhaustive dehydroxylation in the montmorillonite lattices.

As the amount of alkali increased, the band at 1035 cm^{-1} progressively shifted towards a higher frequency at 1042 cm^{-1} overlapping the adjacent band at 1081 cm^{-1} with 6% CaO, and then towards a lower frequency at 1030 cm^{-1} with 50% CaO, giving one single, broader band. This suggests that more Ca^{2+} ions reacted with the tetrahedrons of the montmorillonites.

The bands at 3410 and 1630 cm^{-1} decreased with an increase in the amount of alkali but remained moderately, indicating the presence of preferable hygroscopicity or an appropriate surface activity as well as the formation of CSH.

For the same composition of alkali, the amount of CSH estimated from the intensities of the bands at 855 and 1480 cm^{-1} was found to be greater than in the corresponding filler calcined at 400 °C for 1.5 hr, whereas that of the calcite (1425, 875, and 715 cm^{-1}) formed fairly less. Therefore the thermal treatment (600 °C, 1—1.5 hr) is considered to be more advantageous for the production of CSH than in the lower-temperature calcination. The formation of CSH on the lamellae surfaces of the montmorillonites could restrain the excessive contraction, sintering and/or partial fusion of the minute crystallites induced by the calcination (600 °C, 1—1.5 hr). Thus the facilitation of disintegrating the calcined products resulted in the reduction of both the particle size and its distribution of the fillers prepared.

(iii) Calcination at 800 °C for 1—1.5 hr (Fig. 2 (c)). The bands at 3650, 914 and 835 cm^{-1} disappeared completely in the fillers prepared with or without alkali followed by the calcination (800 °C, 1—1.5 hr) and mechanical disintegration.

No phase attributable to the pyrophillite dehydroxylate, which was observed in the calcined **N** (600—800 °C, 1 hr), appeared in the fillers treated with hydrated lime (3—50% CaO) and by the subsequent calcination (800 °C, 1—1.5 hr) and mechanical disintegration. The restraint of forming the pyrophillite dehydroxylate might be resulted from the presence of the CSH distributed on the lamellae surfaces of the montmorillonites.

As the amount of alkali increased, the band at 796 cm^{-1} decreased with noticeable broading and still remained the intensity even with 50% CaO. Further polycondensation of the excess silica can be suggested under the conditions of preparation.

The bands at 1081, 1033 and 914 cm^{-1} overlapped each other, giving a very broad band around 1020 cm^{-1}. A considerable amount of Ca^{2+} ion might be incorporated into the octahedrons as well as the tetrahedrons of the montmorillonites by the calcination. Under such a high-temperature calcination, sintering or partial fusion of the minute crystallites should coincidently be accompanied in the fillers treated with higher composition of alkali. This should result in lowering the pulverizability of the prepared fillers due to the formation of too hard aggregates to be disintegrated.

The bands ascribable to CSH (1480 and 855 cm^{-1}) showed the intermediate intensities of the respective peaks observable in the fillers calcined at 400 and 600 °C for 1—1.5 hr, whereas the amount of calcite decreased noticeably with less than 30% CaO. A partial decomposition of calcite and the migration of $CO_3{}^{2-}$ ion into the lattices of the newly formed minerals may be suggested.

The results obtained substantially agreed with those investigated by X-ray diffraction.

(2) Physicochemical Properties. *(i) Hygroscopicity*: Figure 3 (a) demonstrates obviously that the more the amount of alkali and the higher the temperature of calcination, the greater the effect of lowering the hygroscopicity of the fillers obtained.

A hyperbolic decrease in the hygroscopicity with an increase in the amount of alkali appeared in those treated with hydrated lime (CaO 3—60%) followed by the calcination (400—600 °C, 1—1.5 hr) and mechanical disintegration. The decreasing rate with respect to the change of the same amount of alkali was found to be greater in those calcined at the lower temperature, though the difference was relatively small.

Those prepared with more than 3% CaO and by the subsequent calcination (600 °C, 1—1.5 hr) and mechanical disintegration gave the hygroscopicity smaller than half of that (15.08%) of the dried **N**. Even those treated with more than 25% CaO followed by the calcination (400 °C, 1.5 hr) and mechanical disintegration would afford the values less than that (8.4%) of Silene EF.

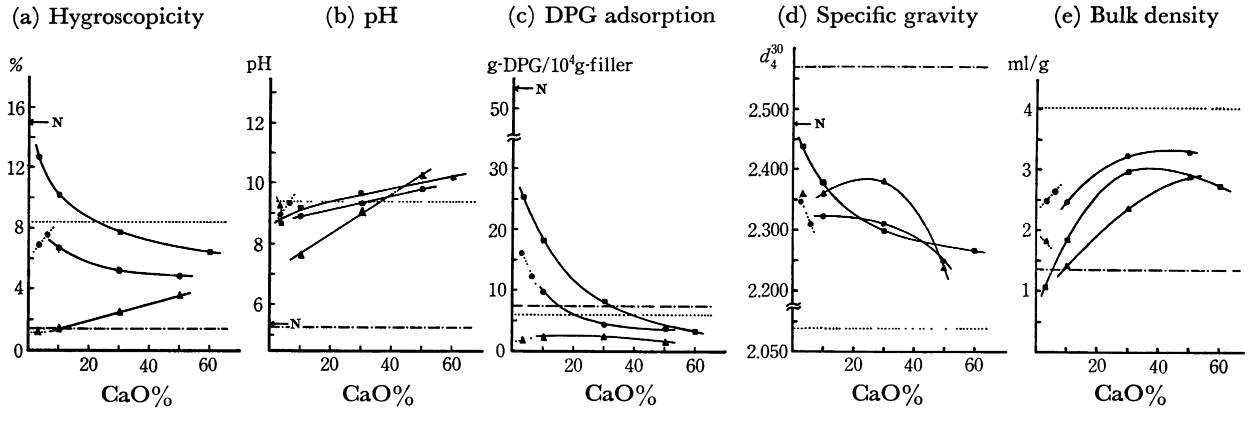

(a) Hygroscopicity (b) pH (c) DPG adsorption (d) Specific gravity (e) Bulk density

Fig. 3. Physicochemical properties of **N** hard clay (CaO 3—60%; calcination 400—800 °C, 1—1.5 hr; mechanical disintegration 18 hr) as compared with those of Dixie Clay, Silene EF and dried **N**. (a): Hygroscopicity, (b): pH, (c) DPG adsorption, (d) Specific gravity, (e): Bulk density.
▲……▲ 800 °C, 1.5 hr; ●……● 600 °C, 1.5 hr; ■——■ 400 °C, 1.5 hr; ▲——▲ 800 °C, 1 hr; ●——● 600 °C, 1 hr; —·—·— Dixie Clay; …… Silene EF.

A noticeably-decreased hygroscopicity comparable to that (1.46%) of Dixie Clay was obtained in those prepared with less than 10% CaO and by the subsequent calcination (800 °C, 1—1.5 hr) and mechanical disintegration. Whereas the values conversely increased in proportion to an increase in the amount of alkali up to 50% CaO. The peculiar phenomenon may be attributed to the formation of some basic calcium salts (CaO/SiO_2 and/or $CaO/Al_2O_3>1$) during the course of the high-temperature calcination: A remarkable increase in pH, the lowest values in DPG adsorption and changes in the specific gravity and bulk density discussed later are considered to be the verifications in reference to the results investigated into the fillers by the X-ray diffraction and IR spectroscopy.

(ii) pH: Figure 3 (b) illustrates changes in the pH of **N** hard clay. The pH (5.40) of the dried **N**, slightly greater than that (5.30) of Dixie Clay, varied noticeably with the treatment with alkali (CaO 3—60%) followed by the calcination (400—800 °C, 1—1.5 hr) and mechanical disintegration (wet milling 18 hr), and resulted in the pH values comparable to that (9.45) of Silene EF in the fillers prepared.

Those treated with alkali (CaO 10—60%) and by the subsequent calcination (400—600 °C, 1—1.5 hr) and mechanical disintegration gave a proportional increase in the pH values with an increase in the amount of alkali. For the same composition of alkali, a high-temperature-calcined product showed a smaller value (about 0.3) than in the one treated by a lower-temperature calcination. This indicates that the higher-temperature calcination (600 °C, 1—1.5 hr) caused a further fixation of dissociative Ca^{2+} ions in the minute crystallites of the fillers.

Those prepared with alkali (CaO 10—50%) followed by the calcination (800 °C, 1 hr) and mechanical disintegration afforded an abrupt but proportional increase in the pH values as the amount of alkali increased. Formation of some basic calcium salts in the matrix can also be suggested on the basis of the followings; (1) a basic calcium salt, which generally exhibits a greater pH value than that of a normal one, is easily produced under the conditions of treatment with more alkali and by higher-temperature calcination, (2) no signal related to $Ca(OH)_2$ was observed in the fillers by means of X-ray diffraction and IR spectroscopy and (3) the results investigated on the structural changes previously described.

In the case of those produced with 3% CaO followed by the calcination (400—800 °C, 1.5 hr) and mechanical disintegration, the pH values appeared in a reverse order as compared with those treated with more than 10% CaO mentioned above. Although the difference of pH among the fillers were relatively small, they increased the values with an increase in the temperature of calcination. Presumably the formation of localized basic salts might be predominant under the conditions of preparation with such a little amount of alkali as 3% CaO followed by the calcination at a sufficiently high temperature.

(iii) DPG Adsorption: Figure 3 (c) shows changes in the DPG adsorption of **N** hard clay. A hyperbolic decrease in the DPG adsorption analogous to the hygroscopicity described above appeared in the fillers (CaO 3—60%; calcination 400—600 °C, 1—1.5 hr; wet milling 18 hr). The higher the temperature of calcination, the greater the effect of decreasing the DPG adsorption or the surface activity of the filler obtained. However, the decreasing rate with respect to the change with the same amount of alkali was found to be greater in the filler prepared with a less amount of alkali followed by calcination at a lower temperature.

The great DPG adsorption of the dried **N** (53.44 g DPG/10^4 g filler) would diminish to the degree comparable to or even less than those of Dixie Clay (6.05 g DPG/10^4 g filler) and Silene EF (5.08 g DPG/10^4 g filler) by the treatment with more than 15 (or 35)% CaO and by the subsequent calcination at 600 (or 400) °C for 1—1.5 hr and mechanical disintegration.

Those prepared with alkali (CaO 3—50%) followed by the calcination (800 °C, 1—1.5 hr) and mechanical disintegration decreased the values as low as 1/2 of that of Silene EF. They remained the values nearly unchanged irrespective of the variation in the amount of alkali. This indicates that the surface activity of the fillers disappeared almost completely.

(iv) Specific Gravity and Bulk Density: Figures 3 (d) and (e) give changes in the specific gravity and bulk density of **N** hard clay, respectively.

A hyperbolic decrease in the specific gravity and a maximum value with about 35% CaO in the bulk density appeared in the fillers (CaO 3—60%; calcination 400 °C, 1.5 hr; wet milling 18 hr).

For the same composition of alkali, however, those prepared with hydrated lime (3—50% CaO) followed by the calcination (600 °C, 1—1.5 hr) and the same mechanical disintegration as above afforded a lower specific gravity and a greater bulk density than those of the former fillers.

The higher the temperature of calcination, the greater the increase in the specific gravity and the decrease in the bulk density of the fillers prepared.

Consequently those treated with alkali (3—50% CaO) and by the subsequent calcination (800 °C, 1—1.5 hr) and mechanical disintegration showed a maximum value in the specific gravity with about 25% CaO and smaller values of the bulk density which increased almost linearly up to 50% CaO. This suggests that sintering occurred in the minute crystallites of the fillers.

The specific gravity (2.3110) and the bulk density (2.65 cc/g) of the best reinforcing filler[2)] derived from **N** were found to be corresponded to the intermediates of the respective values of Dixie Clay (2.5684; 1.38 cc/g) and Silene EF (2.0989; 4.05 cc/g).

(3) Morphology. The prepared hard clays showed small, irregular flake-shaped crystallites, mostly in aggregates, which differ from those[30)] of Dixie Clay and Silene EF; the former being well-formed hexagonal flakes of kaolinite[31)] and the latter being spheroidal-colloid particles in clusters with some elongated lath-shaped units as given in Fig. 4 Plates 2 and 3, respectively.

Plate 1 illustrates the best **N** hard clay (CaO 6%; calcination 600 °C, 1.5 hr; wet milling 18 hr) with the smallest average particle size and its distribution as compared with those prepared under the conditions deviated from the optima. The filler exhibited comparable tensile strength and higher elongation than those of Dixie Clay, though its modulus and hardness were found to be lower than those of the latter.[2]

The average particle size and its distribution of the prepared fillers and the contents of newly formed minerals, CSH, CAH and calcite, were intimately related to the conditions of treatment with hydrated lime followed by calcination and mechanical disintegration besides the mineralogical composition of the original acid clay. A detailed report will be made in comparison with the morphology of **M** hard clay in the next paper.

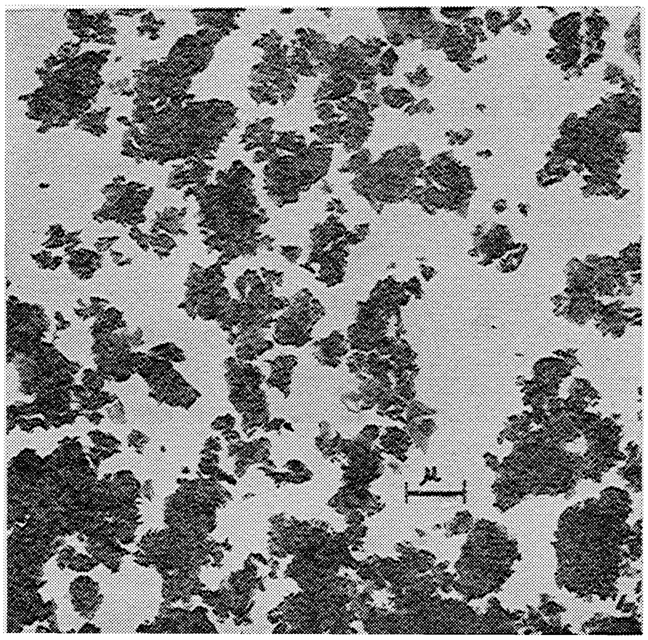


Plate 1. The best **N** hard clay ×9000

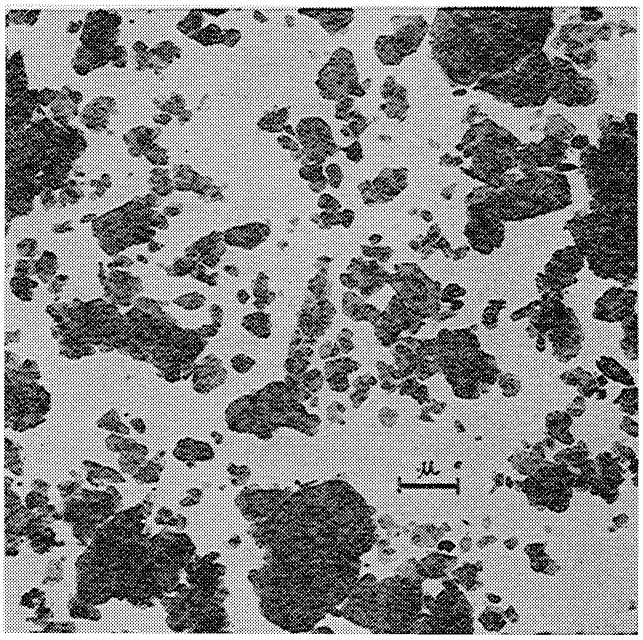


Plate 2. Dixie clay ×9000

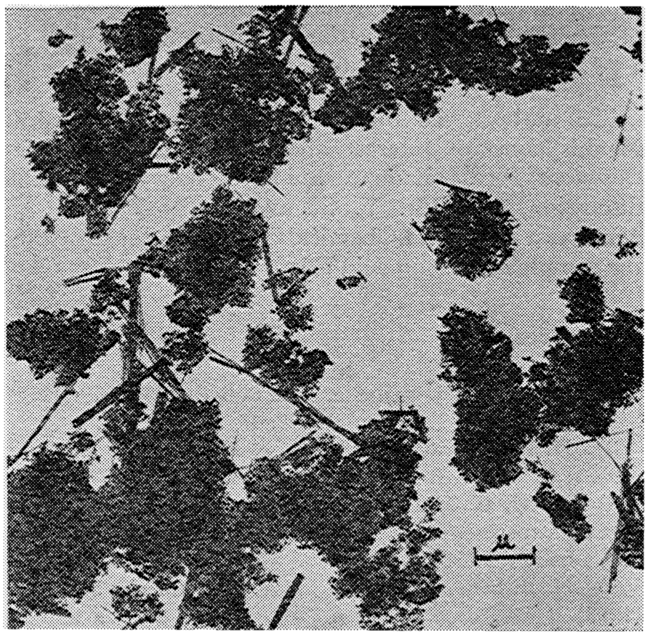


Plate 3. Silene EF ×9000

Fig. 4. Electron micrograph of the best **N** hard clay (CaO 6%; calcination 600 °C, 1.5 hr; wet milling 18 hr) in comparsion with those of Dixie clay and Silene EF.
Plate 1: The best **N** hard clay, Plate 2: Dixie clay, Plate 3: Silene EF.

Conclusion

On the basis of the foregoing investigations on the structure, morphology and physicochemical properties of the fillers together with the results investigated on the reinforcing properties described in the previous paper,[2] it can be unequivocally concluded that the effect on the reinforcement of SBR-1502 compounds agreed precisely with the reduction in both the particle size and its distribution of the fillers.

The treatment with an optimum amount (CaO 6%) of hydrated lime and by the subsequent calcination at an appropriate temperature (600 °C) for a proper time (1.5 hr) and sufficient mechanical disintegration (wet milling 18 hr) caused a favorable change in the structure of **N**. This resulted in an increase in the bulk density and an decrease in the specific gravity of the prepared filler. It simultaneously contributed to restrain the surface properties such as hygroscopicity, pH and DPG adsorption, which were modified to the extent closing to those of Dixie Clay and/or Silene EF.

The treatment with an appropriate amount of hydrated lime followed by proper calcination contributes not only to the formation of CSH and/or CAH on the surfaces of the montmorillonite lamellae, but also to the restraint of thermal effects inducing the excessive, irreversible contraction, unfavorable collapse, sintering and/or partial fusion of the minute crystallites due to the interposition of the newly formed minerals. The collapse, sintering and partial fusion of the calcined products resulted in the formation of too hard aggregates to be disintegrated and the occurrence of a serious breakdown or complete loss in the effective functional groups involved. The inferior reinforcing properties[2] of the fillers treated by the calcination at 800 °C for 1—1.5 hr can be attributed to those reasons.

The authors wish to thank the late Prof. T. Kuwata for his constant interest and encouragement during this work, Prof. J. Kumanotani for his help and valuable discussion, and Mr. Y. Sugawara, the President of Mizusawa Industrial Chemicals Co., Ltd., for providing the sample of Nakajo acid clay.

References

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

2) H. Rai and J. Yamada, *ibid.*, **46**, 3555 (1973).

3) H. E. Swanson and E. Tatge, *NBS Circular* **539, I**, 58 (1953); ASTM, X-Ray Powder Data File Card 4-0733.

4) D. M. C. MacEwan, "The X-ray Identification and Crystal Structures of Clay Minerals," ed. by G. Brown, Miner. Soc. London (1961), p. 143, 200.

5) H. E. Swanson and E. Tatge, *NBS Circular* **539, I** ,39 (1953).

6) G. R. Glenn, *J. Amer. Ceram. Soc.*, **50**, 312 (1967).

7) H. F. W. Taylor, "Progress in Ceramic Science," Vol. 1, ed. by J. E. Burke, Pergamon Press (1961), p. 89.

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

9) L. Heller, V. C. Farmer, R. C. Mackenzie, B. D. Mitchell, and H. F. W. Taylor, *Clay Mineral Bull.*, **5**, 56 (1962).

10) E. C. Jonas, *Natl, Acad, Sci., Publ.*, **395**, 66 (1955).

11) R. E. Grim and W. F. Bradley, *Amer. Mineral.*, **33**, 50 (1948).

12) W. F. Bradley and R. E. Grim, *Amer. Mineral.*, **36**, 182 (1951).

13) R. E. Grim and W. F. Bradley, *J. Amer. Chem. Soc.*, **23**, 242 (1940).

14) L. S. Wells, W. F. Clarke, and H. F. McMurdie, *J. Res. Natl. Bur. Stand.*, **30**, 367 (1943).

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

16) V. Stubičan and R. Roy, *Amer. Mineral*, **46**, 32 (1961).

17) V. Stubičan and R. Roy, *Zeit. Krist.*, **115**, 200 (1961).

18) B. D. Mitchell, V. C. Farmer, and W. J. MacHardy, *Advan. Agr.*, **16**, 349 (1964).

19) E. R. Lippincott, A. V. Valkenburg, C. E. Weir, and E. N. Bunting, *J. Res. Natl. Bur. Stand.*, **61**, 61 (1958).

20) M. Field, I. K. Walker, and P. P. Williams, *New Zealand J. Sci. Technol.*, **38**, 31 (1956).

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

22) K. Fukui, *J. Soc. Rubber Ind. Japan*, **37**, 858 (1964).

23) E. Suito and M. Arakawa, *ibid.*, **34**, 885 (1961).

24) E. E. Angino, *Amer. Mineral.*, **52**, 137 (1967).

25) C. E. Weir and E. R. Lippincott, *J. Res. Natl. Bur. Stand.*, **65A**, 175 (1961).

26) O. W. Flörke, *Neues Jahrb. Mineral. Monatsh.*, 217 (1953); Veröffentl. *Max-Planck-Inst. Silikatforsch.*, **15**, 11 (1955); *Silicates Inds.*, **26**, 424 (1961).

27) V. Z. Zabelin, *Dokl. Akad. Nauk SSSR*, **139**, 184 (1961).

28) Y. Hirata, *Kogyo Kagaku Zasshi*, **59**, 321 (1956).

29) J. A. Hockey, *Chem. Ind.*, **9**, 57 (1965).

30) E. Suito, M. Arakawa, and H. Hasegawa, *J. Soc. Rubber Ind. Japan*, **26**, 217 (1953).

31) R. E. Grim, "Clay Mineralogy," 2nd Edt., MacGraw-Hill Inc., (1968), pp. 171—174.