Kōgyō Kogaku
Vol. 67, No. 9, pp. 1361-1364, 1964

MINERAL COMPOSITION OF ORES AND SILICAGEL QUALITY

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Translated for

JET PROPULSION LABORATORY
NAS 7-100
1968

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MINERAL COMPOSITION OF ORES AND SILICAGEL QUALITY

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(Received 11 November 1963)

Concerning the acid clay of Nakajo and Odo deposits, their properties as ores and the quality of the activated silica hydrogel obtained from them were measured and the relationship between the two investigated. One result is that the smaller the specific surface area of the acid clay ore, the larger the specific surface area of the activated silica hydrogel obtained from it. Furthermore, the greater the specific surface area of the activated silica hydrogel is, the greater is its reinforcing properties for rubber. As one can judge from the following results of chemical analysis, X-ray diffraction, differential thermal analysis, infrared spectroscopy, and the aromatic adsorption index, acid clays with small specific surface areas, in comparison with those having large specific surface areas, have little cristoballite and a large amount of montmorillonite.

1. INTRODUCTION

Along with the recent increased use of synthetic rubber, it has been noted that fine powder of silicic acid,* or fine powder of silicates which show rubber reinforcing properties almost rivalling carbon black, have been in wide use in the rubber industry under the name of white carbon and the trend in the future is toward an increased need for them. There are many patents† on production methods for powdered silicic acid or powdered silicates, but research reports[1-4] on them are scarce. Usually powdered silicic acid is industrially produced by dissociating sodium silicate with an acid and powdered silicates are produced by a reaction between sodium silicate and a calcium or aluminum salt. Because of the problem of an industrial location which is dependent on a distant overseas source for raw table salt, as is the case with Japan, this method of production, which uses sodium silicate as a raw material, is

*The popular name for powdered silica xerogel

†The following are introductory references concerning production patents
Ono *Ganryō* [*Cosmetics*] *5*, 559 (1961)
Sugehara *Goseigomu* [*Synthetic Rubber*] *2*, 27 (1960)

[1]Oku, Kobayashi *Tōkōshi Hōkoku* [*Tōkōshi Reports*] *48*, 205 (1953)
[2]Oku, Kobayashi " " " " *50*, 140 (1955)
[3]Oku, Takeda " " " " *52*, 431 (1957)
[4]Oku, Nakahara, Kuwabara *Shokuzaikyō* [*Color Resources Cooperation*] *30*, 176 (19

considered economically very impracticable. Consequently, in order to produce powdered silicic acid or silicates domestically, it is hoped that we will utilize through new ideas our silicic resources, which are produced domestically, without the use of sodium.

The acid clay in Japan, which, in its original form, occurs in the form of very fine particles with silicic acid as a main component; this acid clay is deposited underground in what is considered to be an almost inexhaustible supply on the shores of the Sea of Japan, particularly in the prefectures of Yamagata and Niigata. The authors used the silicic acid which in the main ingredient contained in this fine, easily reactive Japanese acid clay and our research on the production of powdered silicates has now extended over several years.

A part of the basic [as opposed to acid] component of the acid clay is dissolved out on treatment with sulfuric acid and its original adsorptivity and contact properties are thereby increased; that is, an activated clay is obtained. Production of this is done industrially. However, if this acid treatment is carried through sufficiently enough, the other components except for silicic acid can be almost entirely removed, and an activated silica hydrogel can be obtained. It is known that if this, in turn, is dessicated, it is easily made into a powder.[5,6] In this report, we have determined the properties of the natural acid clay from the Nakajo and Odo deposits and the quality of the silica hydrogel obtainable from them, and we have also investigated the relationship between the two.

2. METHODS AND RESULTS

2.1 Acid Clay Ores

2.1.1 Method for collecting sample ores. For the acid clay or samples, the two kinds from the Nakajo and Odo deposits in Niigata prefecture, which have high yields, were sampled. The ore deposits of Nakajo and Odo deposits of acid clay are, respectively, located approximately 2 km northeast of the Nakajo station of the Ohetsu main railway lines (Niigata-ken, Kita Kambara-gun, Nakajo-chō) and 3 km south of the Yonegura station of the Akatani railway lines (Niigata-ken, Shin Hatta-shi, Odo).

We considered carefully how to select the test samples from representative places from the clay ore deposits of the Nakajo and Odo regions, and we obtained from the former a light yellow ore (samples No. 1, 2, 3); and from the latter site a light yellow ore (samples No. 6, 7). These ore samples were crushed and, after air drying, were passed through a 100 mesh screen and used as test samples.

2.1.2 Aromatic adsorption index. A determination for each sample was made of their aromatic adsorption index[7] treated in terms of a ratio

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[5]Kuwata, Matsuhara, Sugehara *Tokkōkoku* [*Special Government Bulletin*] (1949) 4115

[6]Kuwata, Matsuhara, Sugehara *Tokkōkoku* [*Special Government Bulletin*] (1949) 4215

[7]Mizutani, Sakada *Kōgyō Kagaku* [*Industrial Chemistry*] *59*, 1399 (1956)

with their specific surface areas. The aromatic adsorption index*—after the samples were dispersed in a mixed solution of toluene 30 [appearance] and iso-octane 70 [appearance] and the toluene had been adsorbed—was expressed as 10^4 times the difference in refractive index before and after adsorption.

In that determination, we added 1 g of the test sample dried at 150°C to 2 ml of the above-mentioned mixed solution, and, after mixing for 2 hours, put it in a centrifuge and obtained the refractive index of the supernatant. The result of these determinations is shown in Table 1. From Table 1 we see that the aromatic adsorption index of the Odo ore (Nos. 6, 7) is greater than that of the Nakajo ores (Nos. 1-5).

Table 1. The chemical composition of Japanese acid clay samples (per cent standard weight of the anhydride)

Sample No.	1	2	3	4	5	6	7
SiO_2	64.62	67.14	71.92	69.66	72.77	75.92	74.09
Al_2O_3	18.24	15.54	14.88	12.85	11.28	12.67	14.33
Fe_2O_3	3.82	3.46	3.77	4.02	2.72	2.56	3.23
CaO	1.00	1.76	1.32	1.30	1.08	0.56	0.66
MgO	6.02	6.64	6.36	5.24	4.07	3.31	2.09
ig loss†	7.13	6.38	3.93	5.93	7.33	4.86	6.26
Total	100.83	100.92	102.18	99.00	99.25	99.98	100.66
$\frac{Al_2O_3}{SiO_2}$ mol	0.166	0.136	0.121	0.108	0.091	0.098	0.114
A.A.I.	11	11	11	12	12	15	15

†loss at 1000°C

2.1.3 Chemical analysis. The results from the chemical analysis of each sample are shown in Table 1. From Table 1, one can see that for the Nakajo ores (Nos. 1-5), compared with the Odo ores (Nos. 6, 7), the alkaline earth metal content, e.g., calcium silicate or manganese silicate, is greater.

2.1.4 X-ray diffraction. The results of X-ray diffraction for each sample are shown in Figure 1. From Figure 1 we note that for each sample, in its ore state, montmorillonite is a very major constituent; also in the Nakajo ore Nos. 1-3, there is quartz present, and in the ores from the same area Nos. 4, 5 as well as in the Odo ore (Nos. 6, 7) —besides quartz—there is a very remarkable cristoballite diffraction line.

2.1.5 Differential thermal analysis. The results of the differential thermal analysis for each sample are shown in Figure 2. We note from

*A.A.I.: abbreviation for Aromatic Adsorption Index.

Figure 2 that the endothermic peaks[8] of 670-700°C and 850-890°C, which are characteristic of montmorillonite and based on OH^- formation, are especially prominent in the Nakajo ores (Nos. 1-3) with the Nakajo ores Nos. 4, 5 coming next; and Odo ores Nos. 6, 7 show one endothermic peak at approximately 670-700°C. Furthermore, an exothermic peak appearing at 900-1000°C is to be found in Odo ores (Nos. 6, 7) at relatively low temperatures, and in Nakajo ores (Nos. 1-5) at around 1000°C. The cause of what we see here is felt to be the difference in quantities of magnesium silicate, the difference in which can be responsible for these effects, and which we feel the latter ores have more of.[9] In addition, endothermic peaks are found at 550°C and 500°C. These were attributed to the silica in the ore (as well as thh quartz, cristoballite, etc.).

2.1.6 Infrared spectroscopy. The infrared absorption spectrum for each sample is shown in Figure 3. In Figure 3, each sample shows the absorption characteristics of montmorillonite.[10] We also see in Nos. 6, 7 the absorption at 1000-1250 cm^{-1} and around 800 cm^{-1} which belong to the frequencies[11] of Si-O which is felt to be due to cristoballite.

2.2 Activated Silica Hydrogel

2.2.1 Method of production. Using the above mentioned seven kinds of acid clay ore samples, activated silica hydrogel was produced through treatment with sulfuric acid. To 250 g of each clay ore (water composition: 45 per cent), after conversion to an anhydride, was added 625 g of 50-percent sulfuric acid. These were placed in conical beakers after twice treating them for 12 hours with the solution heated to 90 ± 2°C. After the samples were washed until all the sulfuric acid was removed, they were dried at 105-110°C and crushed in a Pott [potto] mill and then passed through a 150 mesh screen. The result was taken as the sample.

2.2.2 The characteristics of the samples and comparison against rubber. The characteristics of each sample were determined by the following method.

The volumetric analysis was done by the heretofore traditional method of putting 1 g of the sample in a 50-ml measuring cylinder and shaking it on a desktop until a fixed volume is reached, and then meauring it by the steel cylinder method[12] which makes comparison convenient. The volumetric analysis using the steel cylinder method yields a figure of 1 cm^3 per g under compression with a pressure of 0.05 kg/cm^2.

One g of the sample dried at 105-110°C for two hours was put on a glass plate and refined linseed oil dropped on it from a burette, and kneaded each time with a spatula; when the sample turned into a lump, the quantity of oil was determined.

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[8]Katō *Progress in the study of clays (3)"* Gihōdō (1961), p.13
[9]Sutō *Clay ores,* Iwanami (1953), p.67
[10]Hikata *Kōbutsu [Ores] 4*, 335 (1960)
[11]J.M. Hunt, *et al. Anal. Chem. 22*, 1478 (1950)
[12]Akao *Gomukyō [Rubber cooperation] 31*, 33 (1958)

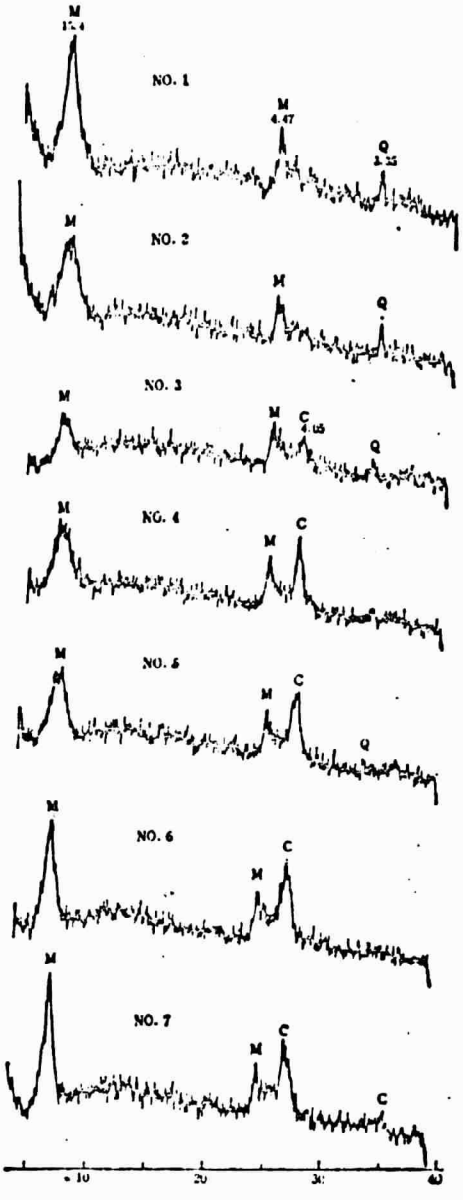
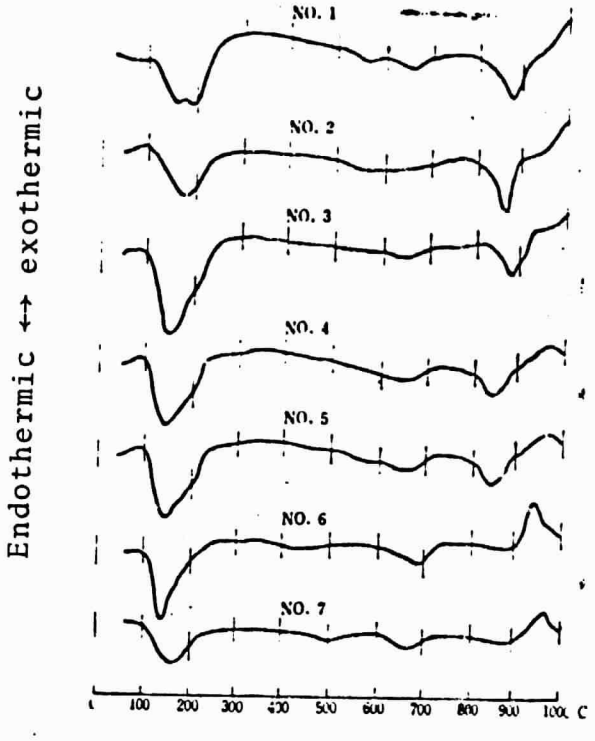


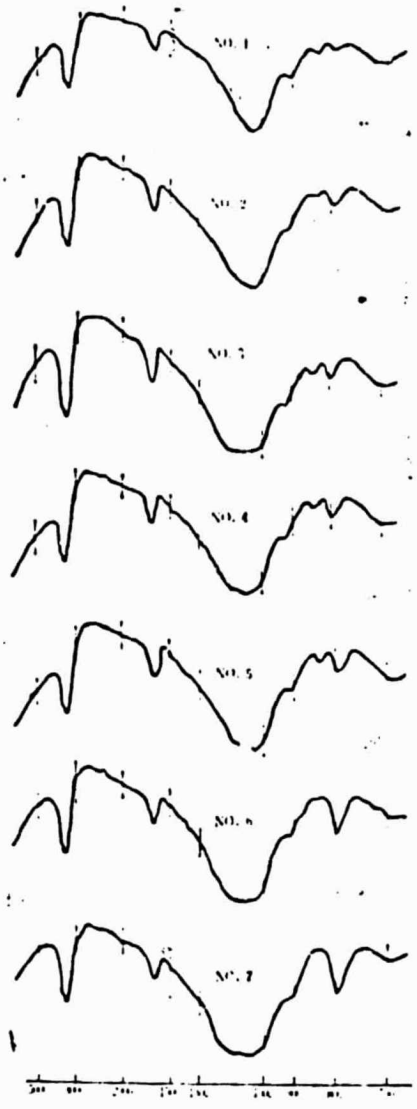
Fig. 1. Graphs of X-ray diffraction lines for acid clay samples

Anticathode: Fe K_α 30 kV 7mA
Scale factor 2
Multiplier 1 Time constant 4 sec
Scanning speed 2°/min chart speed 2°/min
M:Montmorillonite C:Cristoballite
Q:Quartz



Temperature (°C)

Fig. 2. Curves of differential thermal analysis for acid clay samples



Wavelength (cm^{-1})

Fig. 3. The infrared absorption spectra of samples of acid clay

Model: Beckman IR-4 Method of tablet formation (5 mg/700 mg KBr)

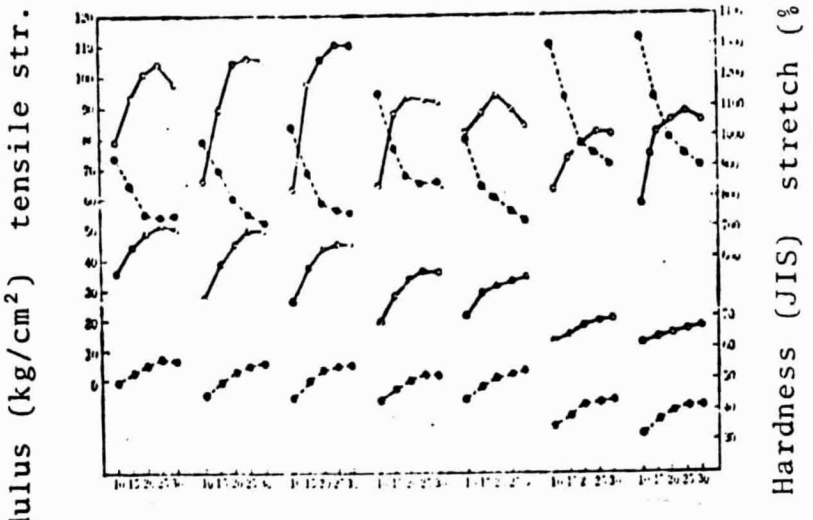


Fig. 4. The strengthening of rubber with fine powder of activated silica

○ tensile strength ◎ Modulus 300%
● stretch ◑ hardness

Composition: SBR 1502 100 zinc oxide 5
stearic acid 1.5 sulfur 2
accelerant DM 1.5
accelerant TT 0.1
diethylene glycol 3
Test sample 60
Vulcanizing temperature
145 ± 1°C

Table 2. Characteristics of test samples of activated silica

Sample No.		1	2	3	4	5	6	7
Water fraction		5.4	5.4	5.6	4.8	5.5	4.8	4.5
Vol. density g/cm	Trad.	0.31	0.30	0.29	0.38	0.38	0.44	0.47
	steel cyl.	0.17	0.17	0.16	0.26	0.28	0.31	0.33
Quan.abs. oil (ml/g)		1.4	1.2	1.1	1.0	0.8	0.7	0.7
A.A.I.		28	26	27	22	21	7.5	9.0
Water number (ml/g)		1.29	1.10	1.10	0.89	0.79	0.48	0.54
chemical compound (%)	SiO_2	94.48	92.03	93.29	95.1[illegible]	95.19	94.44	92.39
	Al_2O_3	0.39	2.17	1.02	0.40	0.58	2.08	2.13
	Fe_2O_3	0.48	0.52	0.40	0.48	0.44	0.50	0.52
	CaO	1.36	0.50	tr	tr	tr	tr	tr
	MgO	0.06	0.05	0.20	0.09	0.14	0.20	0.36
	ig loss	3.60	3.57	4.04	3.88	3.46	3.14	3.61
	Total	100.37	98.84	98.95	100.01	99.81	100.36	99.01

The water number has been reported by Dogadkin *et al.*[13] to be proportional to the specific surface area of fine powders of silicates. One gram of the sample, dried at 105-110°C for two hours, was placed on a glass plate and distilled water was dropped on it from a burette; each time it was mixed with a glass rod, and when the powder turned into a paste, the quantity of water was measured.

For the compound rubber experiment, we used an experimental roller having a 6" x 12" front roller made of the basic compound* and having a rotation speed of 15 rpm and a rotation ratio of 1:1. This roller was used at a temperature of 50-60°C to mix and knead the rubber compound. The vulcanization was done with a steam-heated hand press and the physical test of the vulcanized rubber sheets corresponds to IS-K 6301 (1958).

The characteristics of the test samples, the physical properties of their rubber compounds, and the relationship between the two are shown respectively in Table 2, Figures 4, and 5. The test sample numbers are the same and correspond to the different clay ores. We see from Figures 4 and 5 that the quality of the rubber falls into the order:

*The rubber compound was Japanese Synthetic Rubber [a business] Kakōgijutsu kenkyūjo [Manufacturing Techniques Research Center] *Gomu shiken hō* [*Methods for Rubber Testing*] (1959), p. 14.

[13]B. Dogadkin *et al.* *Rubber Chem. Tech.* *32*, 639 (1959)

Nakajo ores Nos. 1-3, Nakajo ores Nos. 4, 5, and Odo ores Nos. 6, 7; and also we see that there is a relatively good correlation between the characteristics of each kind of ore and the quality of the rubber compound.

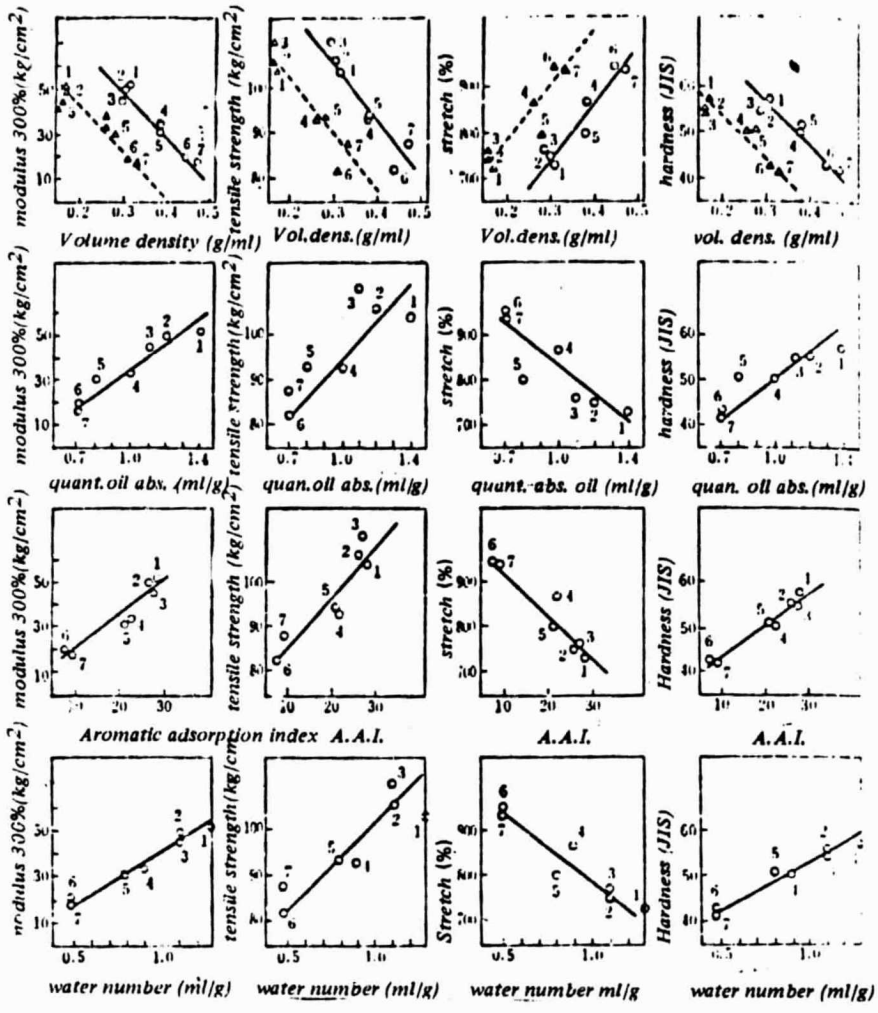


Fig. 5. Relationship between the characteristics of fine powder of activated silica and the properties of rubber

(For the graph of the volumetric analysis, the solid line shows the usual [traditional] method and the dotted line the steel cylinder method)

3. DISCUSSION

In the results of the above experiments there was a correlation between the volume-density, the amount of oil absorbed, the water number, and the aromatic adsorption index, etc. of silica (which are thought to depend on the specific surface area) and the strength of the rubber compounds and this fact indicates that the specific surface area is the main factor in controlling the strengthening of rubber. From the X-ray diffraction, differential thermal analysis, and the infrared spectroscopy,

it was found that those acid clay ores which yield silica gel with large specific surface areas have, as ores, large amounts of montmorillonite and that is one of the main constituents. As far as the cristoballite is concerned, cristoballite is something which crystallizes in silica gel, and, since the original material which had not been turned into silica gel shows it present, those samples which most clearly show cristoballite under X-ray diffraction must have large amounts of it in the silica gel form. We think that the montmorillonite in these samples (Nos. 6, 7) was more hydrogenated than sample Nos. 1-3. We thought that for the silica gel, in order, in part, to encourage the crystallization of cristoballite, we would make the specific surface areas small but that, because we got a greater activation of the montmorillonite, we had in samples Nos. 6, 7, as ores, a large specific surface area. However, in regard to this artificial method, in order to produce noncrystalline silica gel[14] using the acid treatment, we think that one should take material which has large amounts of montmorillonite and produce silica gel which has a large specific surface area.

To summarize the above: Nakajo and Odo ores were used in this report as the test samples and, although the acid clay was produced in the same region, there are great differences in their capacity as additives for strengthening rubber. It has become clear that this is due to differences in the composition of the acid clay.

(10 May 1962, Lectures for the twenty-ninth general meeting of the Cooperative Association for Rubber in Japan (Kanto))

We wish in this report to thank, for their kindness and instruction, Professor Kiyo Morikawa, head of the Chemical Resources Research Laboratory of the Tokyo Technological College and Professor Takaho Shirasaki of the Shitsuran Technical College and Dr. Yūji Egawa of the Agricultural Technology Research Laboratory for giving us instruction in X-ray diffraction, differential thermal analysis, and infrared spectroscopy; and, for cooperation in the experiment, thanks are given to Masaō Nishio, Arata Yahata and Yūjimi Matsumoto of this firm. Also, we would like to thank this company's president Isamujirō Sugewara for authorizing this report.

[14]Maeno *Kōgyō Kogaku* [*Industrial Chemistry*] *67*, 1365 (1964)