

Infrared Studies of Rubber-Filler System.* (I)

Infrared Absorption Spectra of Inorganic Fillers

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Infrared spectra of 33 kinds of commercial reinforcing fillers were measured by use of the KBr pellet method in connection with studies of the filler effect in rubber-filler systems. Characteristic absorptions of individual fillers are discussed in relation to their preparation process.

1. INTRODUCTION

There have already been many infrared studies on elastomers such as natural and synthetic rubber, concerning determination of the molecular structure of polymers, the reaction mechanism in vulcanization and also identification of rubber samples. But few measurements of infrared spectra have been made with rubber in a state loaded with filler. The authors attempted an investigation in rubber-filler system by means of infrared spectra in order to elucidate the filler effect upon the reinforcement of rubber.

The infrared absorption spectra of various types of commercial reinforcing fillers were studied in reference to their preparation process in the present work.

Thereupon the infrared absorption spectra of commercial reinforcing fillers were measured at first.

2. SAMPLE

Fillers submitted to measurement are as follows:

- i. Carbon black : Channel black *Mitsubishi #100*, Furnace black *Seast-I*.
- ii. Colloidal silica : *Aerosil*, *Ultrasil VN-3*, *Durosil*, *Vulkasil-C* (Germany) ; *Valron Estersil*, *Hisil 233* (U.S.A.) ; *Carplex*, *MIKROSIL*, *Tokusil-TP*, *Silmos-A*, *Nisil-F*, *G*, *Vitasil-550* (Japan).
- iii. Calcium silicate : *Calsil*, *Sorlex*.
- iv. Calcium carbonate : *Hakuenka S*, *CC*, *DD*, *U*, (Japan) ; *Supermultifix*, *CaCO₃-L* (U.S.A.) ; *Winnofil* (England).
- v. Calcium Fluoride : *Hinode-Fukkaru*.
- vi. Basic magnesium carbonate : *Tokuso TT*, *Special Chikyu*, *Shionogi AAA*.
- vii. Clays : *Crown Clay*, *Kanpaku Kaolin*, *Hydratex-R*.

3. EXPERIMENTAL

For measurements of infrared spectra of powder samples, the Nujol method

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and the KBr pellet method are used frequently. In some of filler their reinforcing effects have been improved by various surface treatment, the presence of which is observed intensely in the CH vibration in many cases. Since the Nujol method that is used frequently because of its simple procedure is not suitable on account of the overlap of the CH absorptions in Nujol itself and in the surface treatment, the KBr pellet method was adopted in this experiment. The amount of samples were 10% of carbon black, 2mg of colloidal silica, and 5mg of others, each being mixed in 500mg KBr were compressed to pellet under 5 ton/cm² pressure.

The infrared spectra were taken with a Perkin Elmer spectrometer Model-21 and Nihon Bunkō DS 301 spectrometer in the range of 2-15 μ by the use of NaCl prism.

4. RESULTS

The infrared spectra of each filler obtained are shown in Figs. 1~7. The description of each of them will be given below.

i) **Carbon black.** Carbon black is a reinforcing filler most frequently used. Its absorption is so strong that the amount of samples must be much smaller as compared with other fillers. Although the infrared spectra of carbon black have been measured by Hallum¹⁾ *et al.* formerly, no definite result was obtained for the same reason. Because of the difficulty in precise measurement, the spectra were taken with only each one kind of both the channel black and the furnace black.

Fig. 1 (a) shows the absorption spectrum of *Mitsubishi* channel black. The absorption near 2,900 cm⁻¹ was assigned to the symmetric stretching vibration of the CH group, and the absorption at 1,375 cm⁻¹ to the symmetric bending vibration of the CH₃ group. The absorption at 1,613 cm⁻¹ coincides with that of the stre-

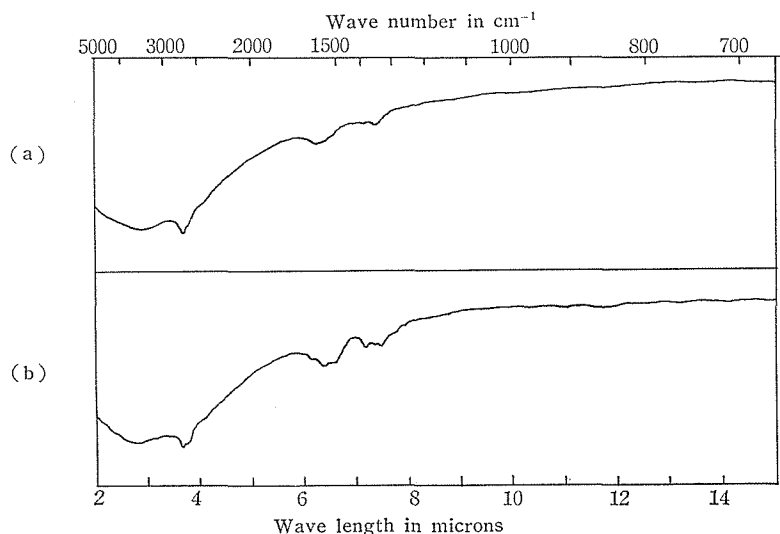


Fig. 1. Carbon black.

(a) *Mitsubishi* # 100 (b) *Seast-I*

ting vibration due to either condensed aromatic ring systems or to hydrogen-bonded conjugated carbonyl groups, which are pointed out by Hallum¹³ *et al*, among the functional groups on the surface of carbon black. These absorptions are also observed similarly in the furnace black in Fig. 1 (b), and the most remarkable difference between both lies in the absorption at 1,550-1,600 cm^{-1} and 1,400 cm^{-1} . This absorption is consistent with those regarded as the symmetrical COO^- vibration, and the fact that this is observed only in channel black is interesting in view of the difference in the methods of preparation.

ii) **Colloidal silica.** This has been important for synthetic rubbers recently, several types are available commercially, and they are classified into following three kinds according to the method of preparation.

- a. Dry method: *Aerosil*.
- b. Wet method, (I) Decomposition of sodium silicate: *Hisil*, *Estersil*, *Ultrasil-VN3*, *Vulcasil-S*, *Durosil*, *Carplex*, *MIKROSIL*, *Tokusil*, *Vitasil*.
- c. Wet method, (II) Byproducts in the production of perphosphate fertilizer: *Nisil-F*, *G*, *Silmos*.

These absorption spectra are classified into three groups slightly different according to the method of preparation as seen in Fig. 2 (a)~(g).

The absorption common to silica consists of a broad and strong absorption at 1,000-1,250 cm^{-1} and a strong absorption²³ at 800-820 cm^{-1} . The absorption at 1,000-1,250 cm^{-1} seems to split into two absorptions having peaks at 1,180 cm^{-1} and 1,100 cm^{-1} respectively. In addition, a somewhat weak absorption exists at 1,650 cm^{-1} . These absorptions are also perceptible in crystalline quartz powders, whereas in crystalline silica a weak absorption is observed at 780 cm^{-1} as seen in Fig. 2 (a).

In *Aerosil* (Fig. 2 (b)) prepared by the dry method, only the OH absorption due to the surface or adsorbed water is observed at 3,200-3,600 cm^{-1} in addition to those absorptions. But in case of *Hisil*, *Vulcasil*, *Durosil* and the similar one produced by the wet method (I) (Fig. 2 (c)) there is a fairly strong absorption at 960 cm^{-1} besides others, whereas in case produced by the wet method (II) (Fig. 2 (g)), this is located at 930 cm^{-1} . Therefore absorptions in the region 1,000 to 1,250 cm^{-1} and 800 to 820 cm^{-1} are the absorptions characteristic to colloidal silica, and the method of preparation can be judged from the existence and position of the absorption at 960 cm^{-1} or 930 cm^{-1} .

Moreover, *Estersil* in Fig. 2 (e) is said to be prepared with an intention to improve the reinforcement by surface active substances adsorbed on the surface of filler. Absorptions which are regarded to be due to the symmetrical and the unsymmetrical stretching vibrations of the CH group and symmetrical COO^- vibration are observed at 2,960 cm^{-1} , 2,900 cm^{-1} , and at 1,460 cm^{-1} respectively and thus the existence of surface treating agents is obvious.

iii) **Calcium silicate.** There are sharp bands at 856 cm^{-1} , 1,500 and 1,540 cm^{-1} in addition to the absorption due to silicate at 1,000 cm^{-1} -1,250 cm^{-1} and 800 cm^{-1} . (Fig. 3 (a), (b)). The bands in this region are ones observed with carbonates of both alkali earths such as calcium carbonate which will be cited later and alkalis, but in these samples, the origin of absorptions is obscure. Further, the absorption at 1,640 cm^{-1} , which is seen conspicuously in *Calsil* (Fig. 3 (b)), is due to water.

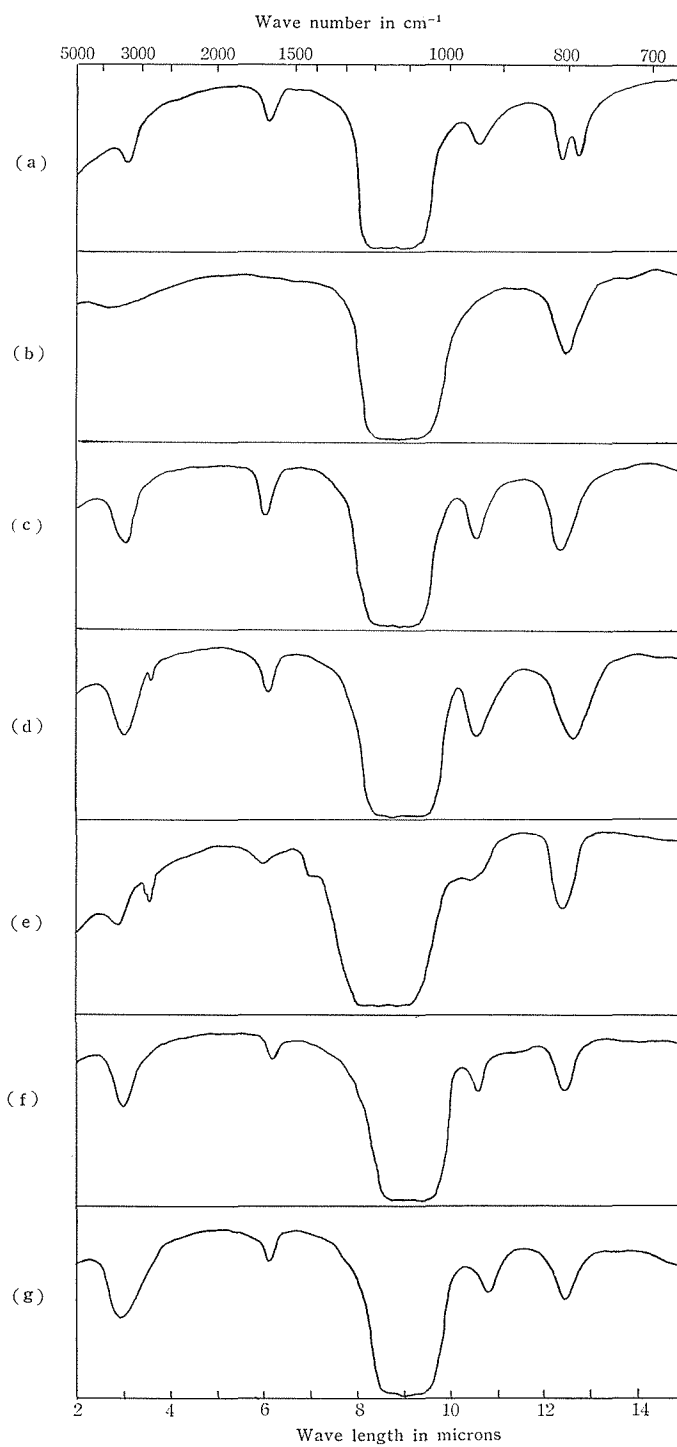


Fig. 2. Colloidal silica

(a) Quartz (b) Aerosil (c) Hisil 233, Vulkasil-S, Durosil (d) Ultrasil VN-3 (e) Valron Estersil (f) Carplex, MIKROSIL, Tokusil-TP, Vitasil 555 (g) Nisil F, G, Silmos

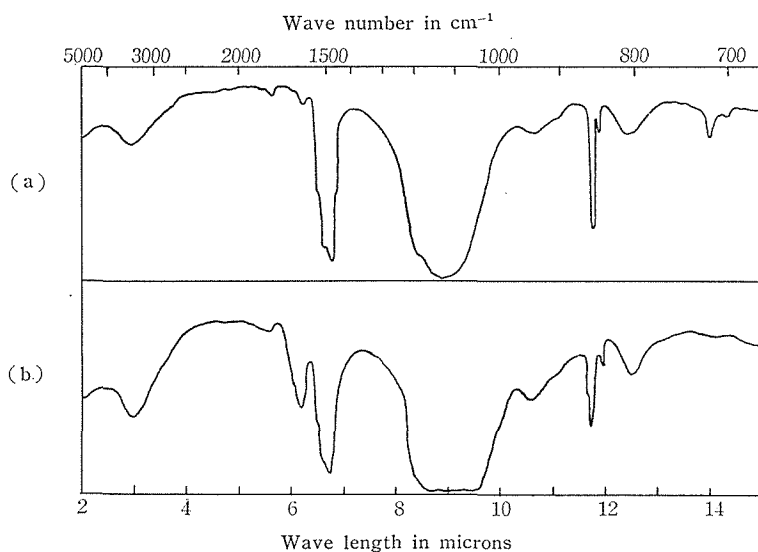


Fig. 3. Calcium silicate

(a) *Sorlex* (b) *Calsil*

iv) **Calcium carbonate.** As shown in Fig. 4 (a)~(f), those observed commonly for each sample are weak band at 2,500, 1,795, 1,400–1,550, 875, 849 and 715 cm^{-1} . Among them those in the region 1,400 to 1,550 cm^{-1} and 875 cm^{-1} are the absorption due to CO_3^{--} which is common to carbonate, and they are also observed³⁾ for carbonate not only of alkaliearths metals but also of cobalt, lead, iron and so on. The characteristic of calcium carbonate is the absorption at 715 cm^{-1} and 849 cm^{-1} . Especially the absorption at 715 cm^{-1} is useful in distinguishing between Calcite and Aragonite, two crystalline forms of calcium carbonate, and Aragonite has a somewhat weak absorption at 705 cm^{-1} .⁴⁾ Precipitated calcium carbonate produced by the so-called soda method (in U.S.A.) in Fig. 4 (f) was found to contain Aragonite, although it is not used for rubbers, and its existence was confirmed by X-ray. Every calcium carbonate for rubbers takes a crystalline form of Calcite.

Most fillers of calcium carbonate are coated by surface active agent and naturally these can be surmised with respect to the kind of treating agent. It is more accurate, to extract such a agent from sample powders with a suitable procedure for the identification of surface treating agent, but intact powder sample itself can also be used for of measurement. In Fig. 4 (b) *Hakuenka* CC, shows the absorption due to the CH stretching vibration at 2,940 and 2,880 cm^{-1} and the COO^- unsymmetric stretching at 1,590 cm^{-1} , from which the surface treatment by fatty acid can be inferred. *Supermultifix* and *Winnofile* (Fig. 4 (e)) are also thought to have received a similar treatment. As for *Calmos* (Fig. 4 (d)), other kinds of treating agents are presumed, because the absorption at 2,940 cm^{-1} is not observed.

Regarding studies on mechanism of surface treatment for such powders by infrared absorption spectra, another communication will be made elsewhere.

v) **Calcium fluoride.** Calcium fluoride given in Fig. 5 is obtained as a bypro-

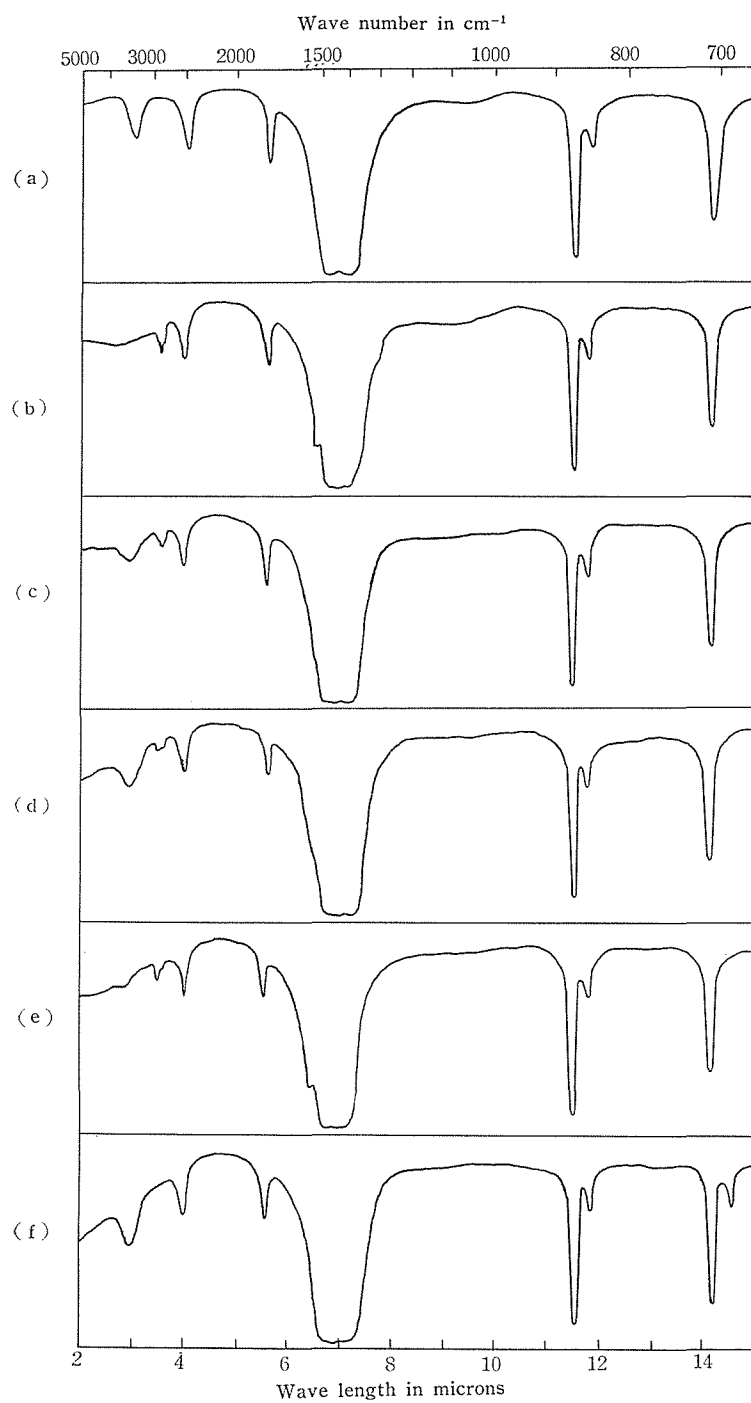


Fig. 4. Calcium carbonate

(a) *Hakuenka S* (b) *Hakuenka CC*, (c) *Hakuenka DD, U*, (d) *Calmos*,
 (e) *Supermultifix, Winnofil*, (f) $\text{CaCO}_3\text{-L}$

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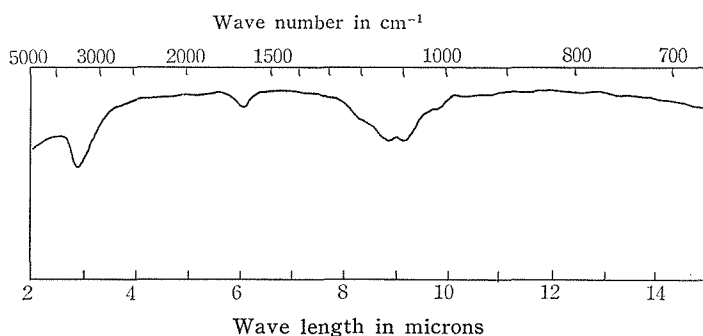


Fig. 5. Calcium fluoride, *Hinode Fukkaru*.

duct in the production of phosphate manure, consisting of ultrafine particles, and tests for rubber fillers have been carried on. Pure calcium fluoride does not show any absorption at all in the range of wave length (2-15 μ), but as this sample is an industrial product, absorption bands presumably due to a impurity SO_4^{--} exist at 1,150 cm^{-1} and 1,080 cm^{-1} .

vi) **Basic magnesium carbonate.** Basic magnesium carbonate used as a filler for transparent rubber has an absorption of CO_3^{--} group, which is separated into absorptions at 1,430 cm^{-1} and 1,500 cm^{-1} as seen in Fig. 6 (a) (b) and the fairly strong absorption at 800 cm^{-1} is characteristic. As for *Special Chikyu* and *Shionogi AAA*, the absorption at 855 cm^{-1} is weak and in addition to this, absorptions of CaCO_3 are noticed at 875 cm^{-1} , 720 cm^{-1} , 1,800 cm^{-1} , and 2,520 cm^{-1} .

vii) **Clays.** Absorptions of Hard clay (*Crown clay*), Soft clay (*Hydratex*), and *Kanpaku Kaolin* are shown in the Fig. 7 (a)~(c). The Si-O absorption band in the regions 1,030 to 1,250 cm^{-1} , which well resembles that in case of silica, shifts to longer wave length and is located at 980-1,100 cm^{-1} ,²⁾ and a fairly strong

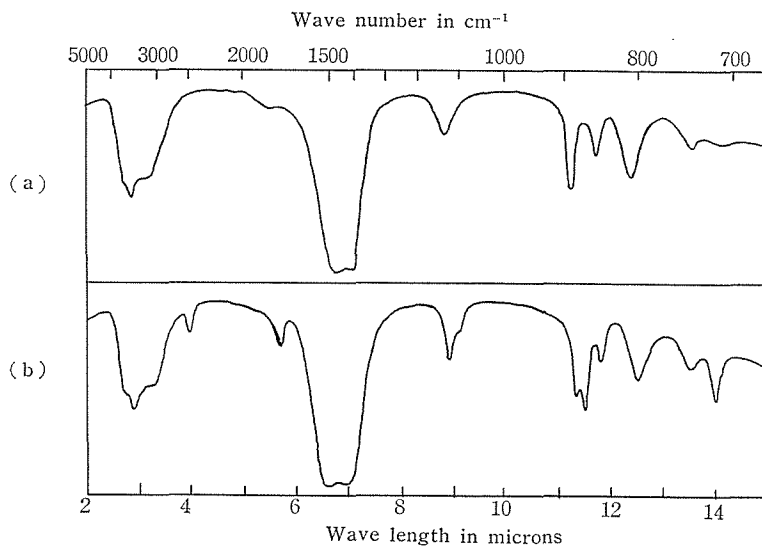


Fig. 6. Basic magnesium carbonate

(a) *Tokuso TT* (b) *Special Chikyu Shionogi AAA*

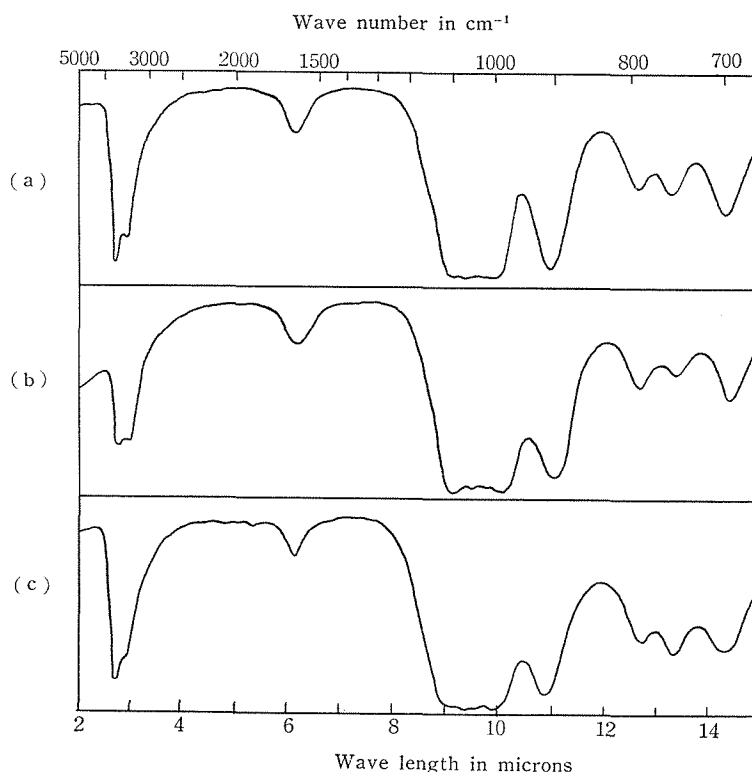


Fig. 7. Clays

(a) *Crown clay* (Hard clay). (b) *Kanpaku Kaolin* (c) *Hydratex-R* (Soft clay)

absorption at 910 cm^{-1} along with three absorptions between $680\text{--}800\text{ cm}^{-1}$ is characteristic of Kaolin. As it was reported²⁾ that montmorillonite has a similar absorption but talc (magnesium silicate) and albite ($\text{NaAlSi}_3\text{O}_8$) have only an absorption at $980\text{--}1,100\text{ cm}^{-1}$ and no absorption is observed at 910 cm^{-1} , the unique band of minerals belonging to alumina silicate series should be at 910 cm^{-1} .

5. CONCLUSION

Infrared absorption spectra of various kinds of reinforcing fillers were measured. Since absorption spectra vary according to the difference not only in chemical composition but also in the method of preparation or crystalline form, the unique absorption bands to each sample were investigated. As the result, as will be given in reports following this paper, the identification of fillers as well as the kind of rubbers was made possible by measuring the infrared spectra of rubbers compounded with fillers.

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REFERENCES

- (1) J. Hallum, H. V. Drushel, *J. Phys. Chem.* **62**, 109 (1958).
- (2) J. M. Hunt, M. P. Wisherd and L. C. Bonham, *Anal. Chem.*, **22**, 1478 (1950).
- (3) F. A. Miller, C. H. Wilkins, *Anal. Chem.* **24**, 1253 (1952).
- (4) J. M. Hunt, D. S. Turner, *Anal. Chem.*, **25**, 1169 (1953).