

Infrared Spectroscopic Studies of Ultrathin Microtomed Sections of Polymers. Part II. Characterization of Both Fillers and Rubbers in Cured Rubbers Loaded with Inorganic Fillers

P. J. CORISH

Chemical Research Department, Central Research Division, Dunlop Research Centre, Birmingham, England

INTRODUCTION

A previous paper¹ has described the use of ultrathin microtomed sections for polymer identification in vulcanized black-loaded rubbers. The technique has been used subsequently for examination of many samples containing inorganic fillers in place of, and in addition to, carbon black. It was found that a great deal of useful information could be obtained from such spectra; filler identification, in addition to polymer recognition, could be carried out.

This paper describes the infrared spectroscopic examination of most of the inorganic fillers used in rubbers and puts future identification of fillers in vulcanizates on a much sounder footing. It has been stimulated by previous publications describing infrared spectra of inorganic compounds.²⁻⁴

The work described in this paper represents an alternative to previous methods for examination of polymers and fillers in vulcanized rubbers which involve tedious, difficult, and time-consuming separation of filler by dissolution of the polymer in high-boiling solvent.⁵⁻⁶

EXPERIMENTAL

Infrared spectra of all the more common inorganic fillers used in the rubber industry were obtained, for the most part by means of the potassium chloride disk technique. A few fillers, such as titanium dioxide, zinc oxide, and iron oxide, gave very poor spectra as disks; somewhat better spectra were obtained for the first one in the form of a Nujol mull. The samples of fillers were typical of commercial, factory-used materials.

Spectra of vulcanized rubbers containing inorganic fillers (sometimes plus carbon black) were obtained by means of the ultrathin microtomed sectioning technique described previously.¹ This

involved cutting of microtomed sections of the vulcanized rubbers, ca. 0.5 by 1.5 cm. in area and 2-5 μ thick, and brushing out the sections on to rock-salt plates. The spectra were recorded on a Honeywell-Brown recorder via a scale expansion unit which was able to expand weak absorptions electrically. High loadings of fillers scattered the incident infrared radiation greatly, and it was necessary to use the expanded scale, but rubbers containing low loadings could sometimes be run directly.

RESULTS AND DISCUSSION

Figure 1 shows infrared spectra of all the more common inorganic fillers used in rubbers. Figure 2 displays spectra of some varied vulcanized rubber samples which have been examined by the microtomed section technique.

A. Silica (Crystalline)

Silica fillers have a broad, strong unsymmetrical ν Si—O—Si band from 9.1 to 9.4 μ . Crystalline silica is differentiated from diatomaceous earth (amorphous silica) by its two sharp bands at ca. 12.55 and 12.85 μ and a weaker band at ca. 14.45 μ . Diatomaceous earth has a weak absorption at ca. 12.6 μ only.

B. Calcium Silicate

Calcium silicate has a strong, broad ν Si—O—Si absorption band with a maximum at 9.2-9.5 μ , i.e., at a slightly longer wavelength than silica. In addition, calcium silicate has weakish absorptions at 6.8 and 11.4 μ which enable it to be differentiated from aluminum silicate.

C. Aluminium Silicate

This group of compounds includes Zeolex 23, Manosil AS7, and Bentonite, all of which have very

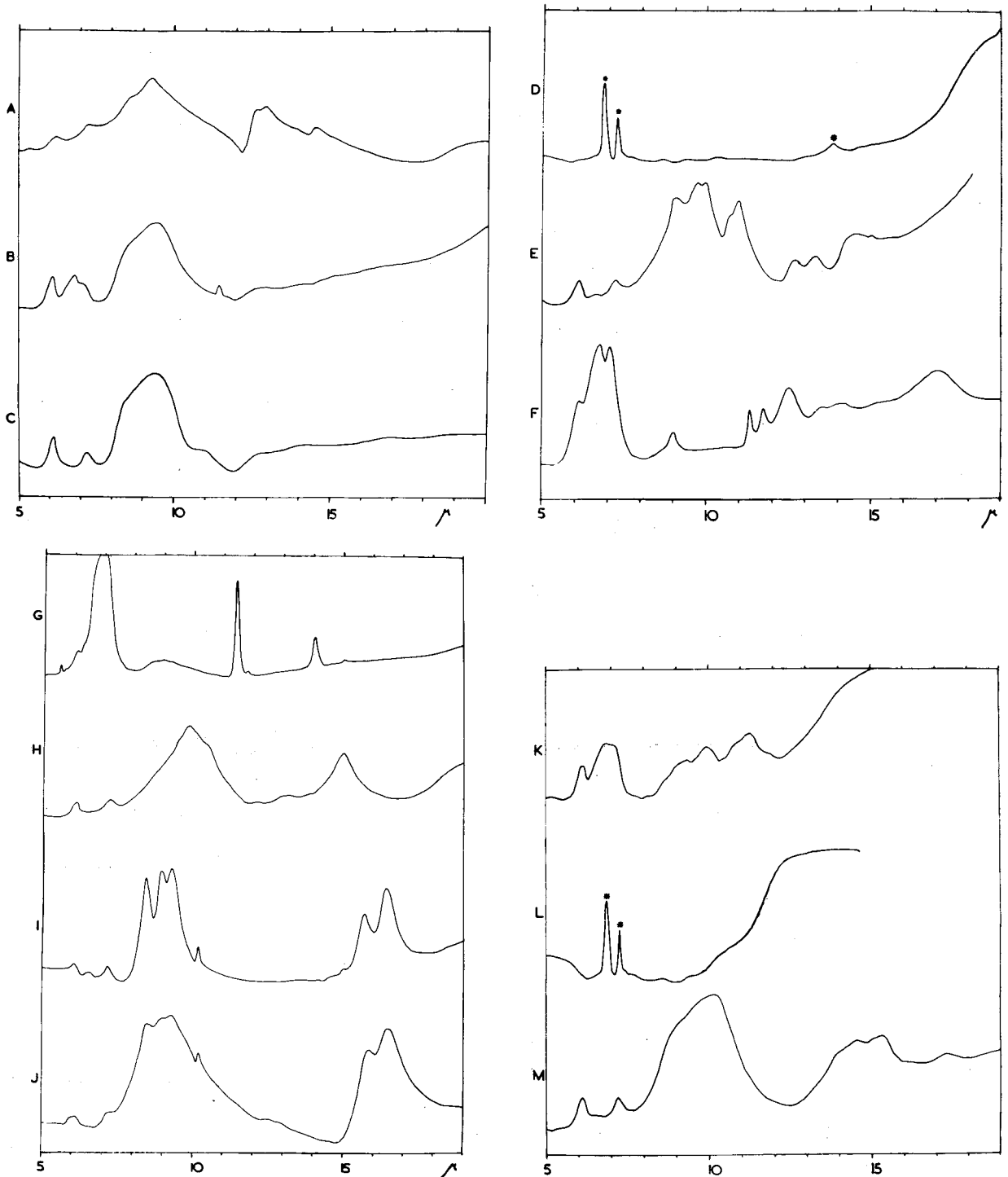


Fig. 1. Infrared spectra of inorganic fillers used in the rubber industry: (A) silica (crystalline); (B) calcium silicate; (C) Zeolox 23 (hydrated aluminium silicate); (D) Zinc oxide (asterisks refer to Nujol absorptions); (E) China clay; (F) magnesium carbonate (light); (G) chalk; (H) French chalk; (I) lithopone; (J) barytes; (K) magnesia (heavy); (L) titanium dioxide (asterisks refer to Nujol absorptions); (M) ultramarine blue. All spectra are of KCl disks except (D) and (L) which are of Nujol mulls.

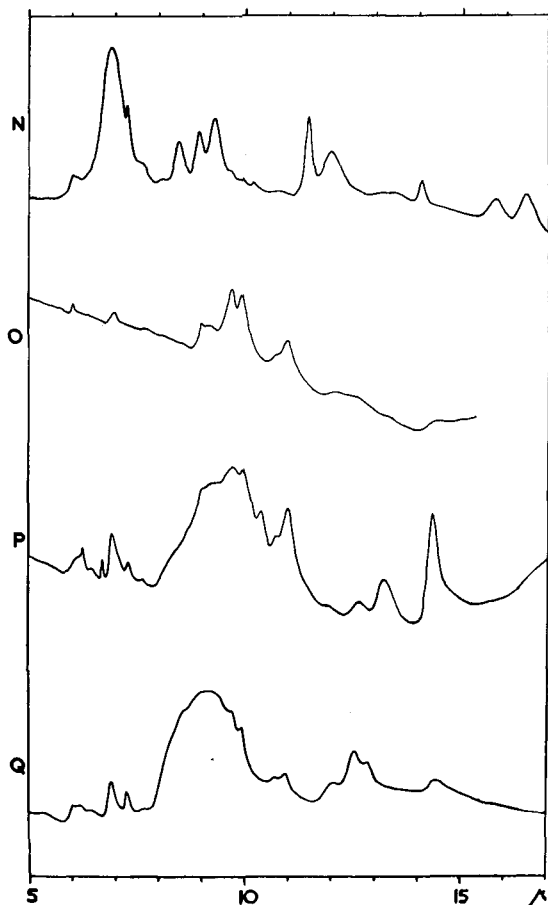


Fig. 2. Infrared spectra of cured rubbers containing inorganic fillers: microtomed sections of (N) cycle tread; (O) black-loaded conveyor belt; (P) underlayer of heel; (Q) moped seat.

similar spectra with a strong broad absorption peaking at 9.2–9.5 μ .

D. Zinc and Iron Oxides

Anhydrous zinc oxide has no specific absorption in the infrared region, as shown by the spectrum of a Nujol mull. This also applies to anhydrous iron oxide.²

E. China Clay (Hydrated Aluminium Silicate)

China clay and Frantex (China clay of French origin) have very similar spectra: both are forms of kaolin, i.e., $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, and differ in their spectra from that of anhydrous aluminium silicate (see above). Absorptions in the 9–11 μ region, viz., at 9.05, 9.73, 9.96, 10.73 (shoulder), and 10.98 μ , are characteristic and distinguish this class of compound from other silicate-type materials.

F. Magnesium Carbonate (Light)

The spectrum of light magnesium carbonate is quite characteristic and corresponds to the published spectrum³ of basic magnesium carbonate, i.e., $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Strong CO_3^{2-} absorptions at 6.75 and 7.05 μ enable this filler to be easily identified.

G. Calcium Carbonate (Activated)

Chalk, whiting, and activated calcium carbonate, forms of calcium carbonate which are widely used as rubber fillers, have very similar spectra. A very strong band due to CO_3^{2-} at ca. 7 μ as well as sharp peaks at 11.43 and 14.07 μ are quite characteristic and different from those present in the spectrum of magnesium carbonate.

H. French Chalk

French chalk is a form of talc, i.e., hydrated magnesium silicate, which has a spectrum with a strong $\nu\text{Si}-\text{O}-\text{Si}$ absorption band at 9.86 μ i.e., at characteristically longer wavelength than for silica, calcium, and aluminium silicates.

A medium absorption at ca. 15.0 μ also serves to differentiate magnesium silicate from other silicate fillers.

I. Lithopone

Lithopone is obtained chemically by coprecipitation of barium sulfate and zinc sulfide and has a very similar spectrum to blanc fixe, i.e., chemically manufactured barium sulfate. Multiple absorption bands in the 8.3–10.3 μ region, viz., at 8.42, 8.94, 9.29, and 10.18 μ , distinguish barium sulfate fillers from other sulfates. The strong pair of bands at 15.75 and 16.47 μ is also very characteristic.

J. Barytes

Barytes, i.e., barium sulfate from mineral deposits, has a very similar spectrum to lithopone and blanc fixe except that the spectrum is less well defined.

K. Magnesia

The two varieties of magnesia, i.e., light and heavy, differ somewhat in spectra, but both do not give very well-defined absorptions in the infrared region. Magnesia (heavy), as shown, has characteristic absorption bands at 6.8–7.1 (broad), 9.35, 9.95, 10.9 (shoulder), and ca. 11.3 μ plus a broadish band rising to cutoff at ca. 14.5–15.0 μ .

The light form of magnesia has a broadish band at ca. 7 μ , a weakish absorption at ca. 9.1 μ , and a very broad band at ca. 14.5–15.0 μ .

L. Titanium Dioxide

The spectrum of titanium dioxide consists of a broad, ill-defined absorption in the 14 μ region. The material tends to scatter infrared radiation, especially when in a potassium chloride disk, so the spectrum is that of a Nujol mull.

M. Ultramarine Blue

Ultramarines are synthetically produced coloured silicates. The spectrum of ultramarine blue confirms this, having a very broad, strong $\nu\text{Si—O—Si}$ absorption peaking at 10.0–10.3 μ , i.e., at a longer wavelength even than magnesium silicate. Medium absorptions at ca. 14.5 and 15.3 μ are also characteristic.

N. Cycle Tread

A cycle tread examined by the use of microtomed sections exhibited absorptions at 6.9, 11.45, and 13.96 μ which can be assigned to the presence of calcium carbonate (see Fig. 1G). Bands at 8.46, 8.92, 9.28, 10.18, 15.75, and 16.45 μ are due to lithopone or blanc fixe (see Fig. 1I). Absorptions at 7.27 μ due to δCH_3 and at 11.98 μ due to $\delta(\text{RCH}=\text{CR}_1\text{R}_2)$ show that natural rubber is present. This information tallies with the known compounding formula of the vulcanizate.

O. Black-Loaded Conveyor Belt

A microtomed section of black-loaded belt gave a spectrum with bands due to "inorganic" filler. These absorptions at 8.96, 9.15, 9.68, 9.92, 10.8 (shoulder), and 10.96 μ are due to the presence of china clay or Frantex (see Fig. 1E). An absorption at 12.13 μ and the absence of a δCH_3 band at 7.27 μ suggested the presence of neoprene.¹ This was confirmed later on removal of filler. The presence of clay explained the easier processing of the compounded rubber.

P. Underlayer of Heel

In the spectrum of a microtomed section of the heel, supplied for analysis, bands due to clay or Frantex were exhibited at 9.0, 9.72, 9.95, 10.7 (shoulder), and 10.98 μ . Absorptions at 10.36 and 10.98 μ due to *trans*-1,4 and 1,2 repeating units occur in polybutadiene, while peaks at 13.23 and 14.35 μ were due to polystyrene units.

The intensity ratio ($R = A_{14.35\mu}/A_{10.36\mu}$) of polystyrene to polybutadiene bands is consistent with the use of a high styrene/butadiene copolymer.

Q. Moped Seat

A microtomed section of a moped seat submitted for analysis displayed a complicated spectrum. Absorption bands at 9.15, 12.55, 12.84, and 14.45 μ were due to crystalline silica (see Fig. 1A) while absorptions at 9.15, 9.7, 9.92, 10.7, and 10.95 μ were due to China clay or Frantex. Additional absorption bands at 6.93 and 7.28 μ due to δCH_2 and δCH_3 vibrations and at ca. 12 μ due to $\delta(\text{RCH}=\text{CR}_1\text{R}_2)$ showed that natural rubber was present. The presence of natural rubber was confirmed by the spectrum of a film after removal of filler.

Only a few examples of the identification of fillers in vulcanizates have been given, but many more could be quoted, as the ultrathin microtomed technique is becoming of increasing importance in examination of vulcanizates. The method is quick and enables a reasonable assessment of both polymer and inorganic filler to be made in a very short time. Occasionally filler absorptions overlap polymer bands, but the identity of the polymer can be confirmed later after removal of the filler:⁵⁻⁶ this, of course, is a tedious procedure.

Previous work on x-ray identification of fillers in vulcanized rubber⁷ is relevant, but only crystalline fillers can be clearly identified. Amorphous fillers are not easy to differentiate by this method.

CONCLUSIONS

Analysis of rubber vulcanizates by chemical methods is rather a lengthy procedure, and the compositions of both polymer and filler are often changed during the processing of the sample.⁵⁻⁶ By means of the method described in this and a previous paper,¹ the identity of both polymer and filler (or sometimes fillers) can usually be found in a very short time. Overlap of filler and polymer absorptions can sometimes lead to difficulties. The technique has been used for examination of a wide variety of products: tires, belting, and many miscellaneous samples. It is hoped to extend the work to consideration of filler/rubber interaction and also to examination of vulcanization mechanisms.

Work is also in progress⁸ on the rapid identification of antioxidant and accelerator residues, which are extracted during the procedure, by use of a

cutting liquid for microtomed sections which is transparent in the ultraviolet region of the spectrum.

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References

1. Corish, P. J., *J. Appl. Polymer Sci.*, **4**, 86 (1960).
2. Harkins, T. R., J. T. Harris, and O. D. Shreve, *Anal. Chem.*, **31**, 541 (1959).
3. Hunt, J. M., Mary P. Wisherd, and L. C. Bonham, *Anal. Chem.*, **22**, 1478 (1950).
4. Miller, F. A., and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).
5. Barnes, R. B., V. Z. Williams, A. R. Davis, and P. Giesecke, *Ind. Eng. Chem., Anal. Ed.*, **16**, 9 (1944).
6. Dinsmore, H. L., and D. C. Smith, *Anal. Chem.*, **20**, 11 (1948).
7. Endter, F., *Kautschuk u. Gummi*, **8**, WT 302 (1955); *Rubber Chem. and Technol.*, **30**, 180 (1957).
8. Corish, P. J., unpublished work.

Synopsis

Many cured, black-loaded rubbers contain varying amounts of inorganic fillers: to characterize the rubber, absorptions due to fillers must be recognized and identified. Reference spectra of all the common inorganic fillers used in the rubber industry have been recorded and their recognition in infrared spectra of ultra-thin microtomed sections of known and unknown samples is described. Both rubbers

and inorganic fillers can usually be identified in cured samples.

Résumé

De nombreux caoutchoucs améliorés, chargés au noir animal, contiennent des quantités variables de matières de remplissage inorganiques: pour caractériser le caoutchouc, on doit pouvoir reconnaître et identifier les absorptions dues à ces matières de remplissage. On a enregistré les spectres de référence de toutes les matières inorganiques de remplissage utilisées dans l'industrie du caoutchouc et on a décrit leur identification par les spectres infrarouges sur des sections ultra-fines (au microtome) d'échantillons connus et inconnus. On peut ainsi identifier simultanément le caoutchouc et son agent de remplissage inorganique dans des échantillons améliorés.

Zusammenfassung

Vulkanisierter, russ-gefüllter Kautschuk enthält in vielen Fällen wechselnde Mengen von anorganischen Füllstoffen: zur Charakterisierung des Kautschuks muss die Absorption des Füllstoffes bestimmt und identifiziert werden. Bezugsspektren von allen üblicherweise in der Kautschukindustrie verwendeten Füllstoffen wurden aufgenommen und ihre Auffindung im Infrarotspektrum ultradünner Mikrotomschnitte von bekannten und unbekanntem Proben wird beschrieben. Sowohl Kautschuk als auch anorganische Füllstoffe können normalerweise in vulkanisierten Proben identifiziert werden.

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