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FOR EVALUATING HIGHWAY MATERIALS
Second Progress Report: Detection and Determination
of Ground, Cured Scrap Rubber in Hot-Poured Joint Sealers



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Second Progress Report: Detection and Determination
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ABSTRACT: New Michigan Department of State Highway Specifications for hot-poured joint sealers require that the material be free from ground, cured scrap rubber, due to its detrimental effect on the ductility and resiliency of the sealer. This report covers the methods of test which were developed in order to enforce this specification. Detection of ground, cured scrap rubber was accomplished in two ways: (1) microscopic investigation of thin films of the sealers by transmitted light to detect particulate matter; and, (2) infrared spectrophotometric analysis of portions of the material soluble in methyl ethyl ketone. The results of analyses of four different joint sealers showed the scrap rubber contents obtained agreed with verbal reports of industry practice. Conclusive data could not be obtained, however, since scrap-free reference samples were unavailable.

KEY WORDS: joint sealers, scrap, rubber, spectrophotometry.

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Introduction

Two general types of hot-poured joint sealers are presently available:

1. A material previously used by the Michigan Department of State Highways, conforming to Federal Specification SS-S-164 which requires only certain physical properties.

2. A new material conforming to a Department specification containing revised flow and bond test requirements and adding ductility and composition requirements. The composition requirements in the 1967 Specifications are as follows: "The material shall be a mixture of natural rubber, or uncured synthetic rubber, or reclaimed rubber, or a combination of these materials, with asphalt, plasticizers and tackifiers. Under no circumstances shall ground, cured rubber scrap be used. The sealing compound shall contain no foreign material, and shall be free from lumps when melted." (The cured rubber scrap is prohibited because of its detrimental effect on the ductility and resilience of the sealer.)

Table 1 compares the physical property requirements for the two types of sealers.

TABLE 1
PHYSICAL REQUIREMENTS

Property	SS-S-164 Federal Specification	New Michigan Specification
Pour Point	at least 20 deg F below max temp	at least 20 deg F below max temp
Penetration at 77 F	0.9 cm in 5 sec	0.9 cm in 5 sec
Flow at 140 F	0.5 cm max	1.0 cm max
Bond at 0 F (5 cycles)	50-percent extension of 1-in. sample	100-percent extension of 1/2-in. sample
Ductility at 77 F	not required	40 cm minimum

Methods of test were needed to enforce the new specification which barred ground, cured rubber scrap. Rubber scrap in joint seal materials

is generally in the form of buffings from discarded tires (1) (GR-S synthetic rubber and some natural rubber). (2) Since preliminary efforts to dissolve the joint sealer in organic solvents to isolate the ground rubber scrap as an insoluble precipitate were not successful, microscopic examination of thin films of sealers to detect suspended particulate matter, and infrared spectrophotometric analysis of the methyl ethyl ketone (MEK) soluble portion of joint sealers were subsequently carried out. The microscopic examination was conceived as a quick screening procedure to determine whether further analysis was required.

Summary

Detection of ground cured rubber scrap in hot-poured joint sealers was accomplished in two ways: (1) microscopic examination of thin films of the joint seals by transmitted light to reveal particulate matter; (2) by infrared spectrophotometric analysis of methyl ethyl ketone (MEK) soluble portions of the joint sealers.

Quantitative estimation of the cured rubber scrap content of four different joint sealers was done by infrared spectrophotometric analysis of the MEK soluble portions. The scrap rubber contents obtained were in agreement with verbal reports of industry practice but could not be conclusively checked because scrap-free blanks were not available.

Experimental Work and Discussion

Solubility Studies

Preliminary efforts to determine ground scrap rubber centered on dissolving the joint sealer in a suitable organic solvent that would dissolve little of the scrap rubber. Solvents such as benzene, carbon tetrachloride, hexane, and 2,2-dimethoxypropane dissolved only 80 to 90 percent of the scrap-free joint sealer. Acetone and MEK dissolved somewhat less of the joint sealer. A sample of cured rubber scrap (tire buffings) was 81.8-percent insoluble in MEK. Further solubility tests on other brands of joint sealer containing cured rubber scrap also indicated that the rubber scrap could not be isolated in this manner.

Some useful observations were made during the solubility testing. As the samples containing cured rubber scrap dissolved, particles of the rubber could be observed upon swirling the solvent. This simple test will detect scrap rubber if it is present in amounts greater than 1 percent by weight.

The suspended particles must still be conclusively indentified as cured rubber. Also, the insoluble residues from various products had different characteristics when dried. If no rubber scrap is present, the dry residue is a rubbery material with a smooth surface. Ground rubber scrap causes a grainy appearance in the residue and lack of elasticity and tensile strength.

Microscopic Studies

Microscopic examination of thin films of five hot-poured joint sealers by transmitted light revealed marked differences in particle content. Three samples of sealer meeting the previously used Federal Specification SS-S-164 contained large numbers of opaque particles, identified as cured rubber scrap, in addition to translucent particles (probably silica). The cured rubber particles ranged from 0.001 to 0.040 in. in largest dimension with the average size being 0.004 in. (Fig 1). The translucent particles averaged 0.005 in. across the largest dimension.

In contrast, Para-Plastic No. 2431, an improved product meeting the Department's 1967 Specification for hot-poured joint sealer, was a relatively homogenous dispersion of very fine opaque particles (smaller than 0.0001 in.) which appeared to be carbon black. Occasional opaque particles 0.0005 to 0.003 in. across and a few translucent particles were also detected (Fig. 2). A film of asphalt viewed for comparison contained no particulate matter whatever.

The fifth joint sealer studied, Presstite No. 357.5, met the physical property requirements but not the composition requirements of the Department's new specification for hot-poured joint sealer. It contained very few large opaque particles, which could be cured rubber scrap or carbon black agglomerates, but numerous translucent particles, probably silica, were observed (Fig. 3). The method of preparing thin films of joint sealer is described in the appendix.

Qualitative Infrared Studies

Infrared spectra of MEK extracts of cured rubber scrap, (in this case, tire buffings), and joint sealers with and without added rubber scrap, indicated that an absorption band near 10.3 microns (due to trans-substituted carbon-carbon double bonds) was characteristic of cured rubber scrap. Extracts of scrap-free joint sealer had little absorption at 10.3 microns. Figure 4 represents infrared spectra of extracts of cured rubber scrap and a scrap-free joint sealer, illustrating the characteristic differences in absorption at 10.3 microns. Thus, absorption of infrared radiation at a wavelength of 10.3 microns can be used to detect cured rubber scrap in joint sealer.

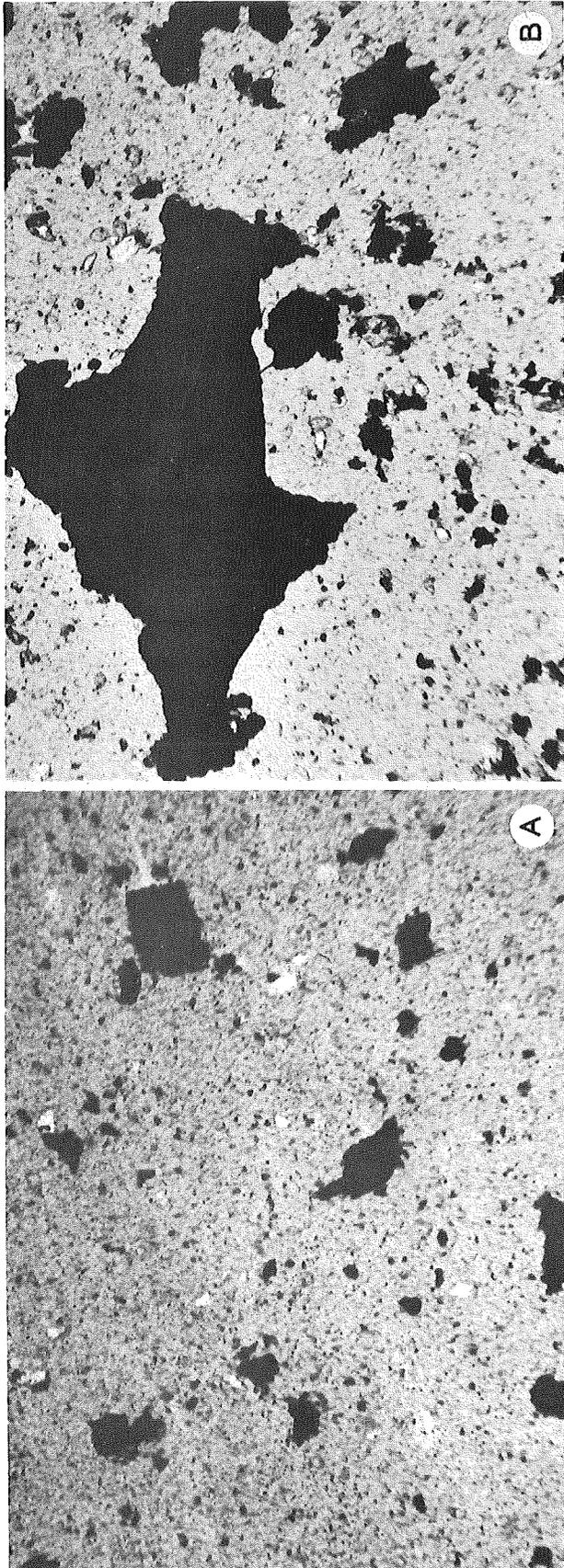


Figure 1. Photomicrographs (90 X magnification) of samples of three hot-poured joint sealers meeting Federal Specification SS-S-164, showing ground cured rubber scrap as dark particles from 0.005 in. (Sample A) to 0.04 in. (Samples B and C) in largest dimension. Lighter, translucent particles, probably silica, also appear.

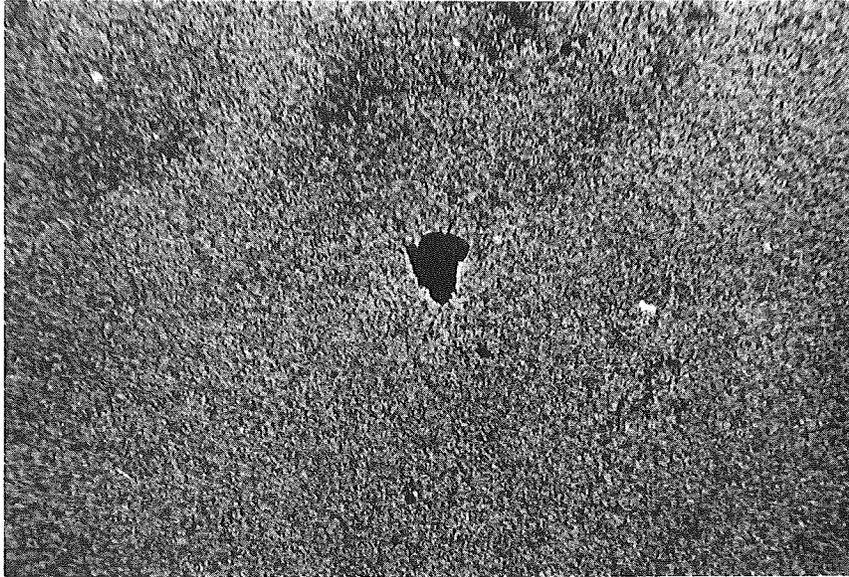


Figure 2. Photomicrograph of scrap-free Para-Plastic No. 2431 joint sealer, showing one of the few larger particles detected (0.003 in.). 90 X magnification.

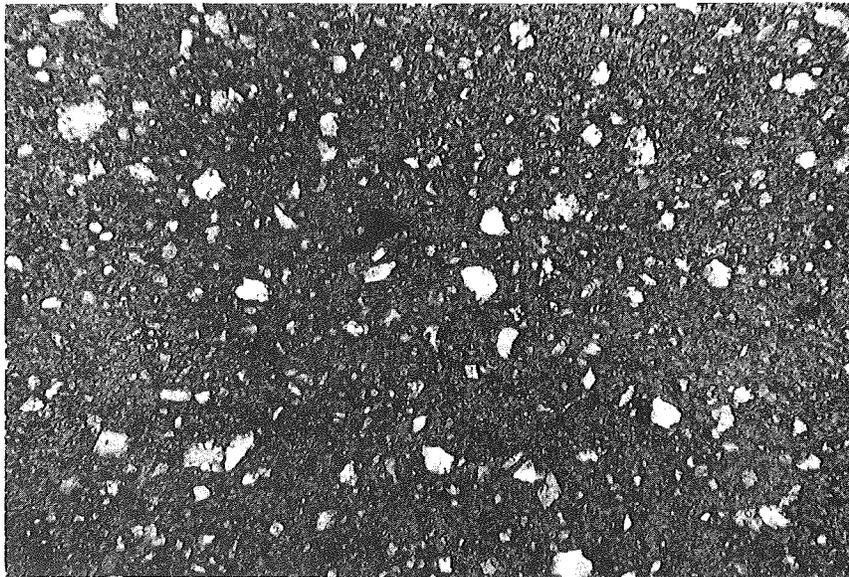


Figure 3. Photomicrograph of Presstite No. 357.5 joint sealer, showing abundant translucent particles and infrequent large, opaque particles. 100 X magnification.

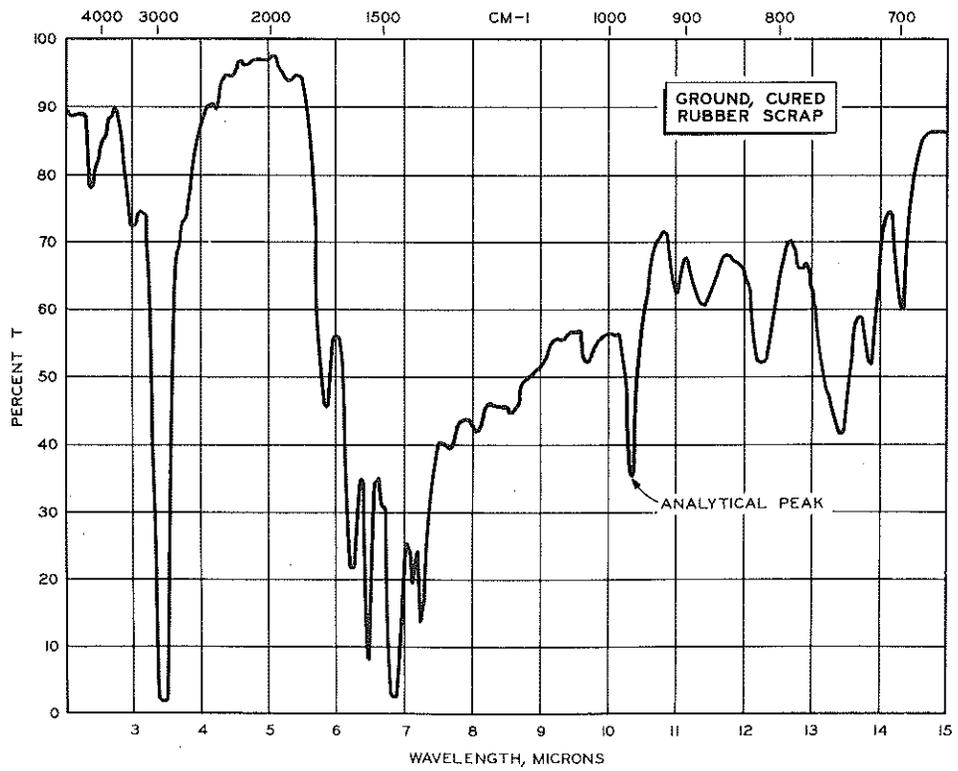
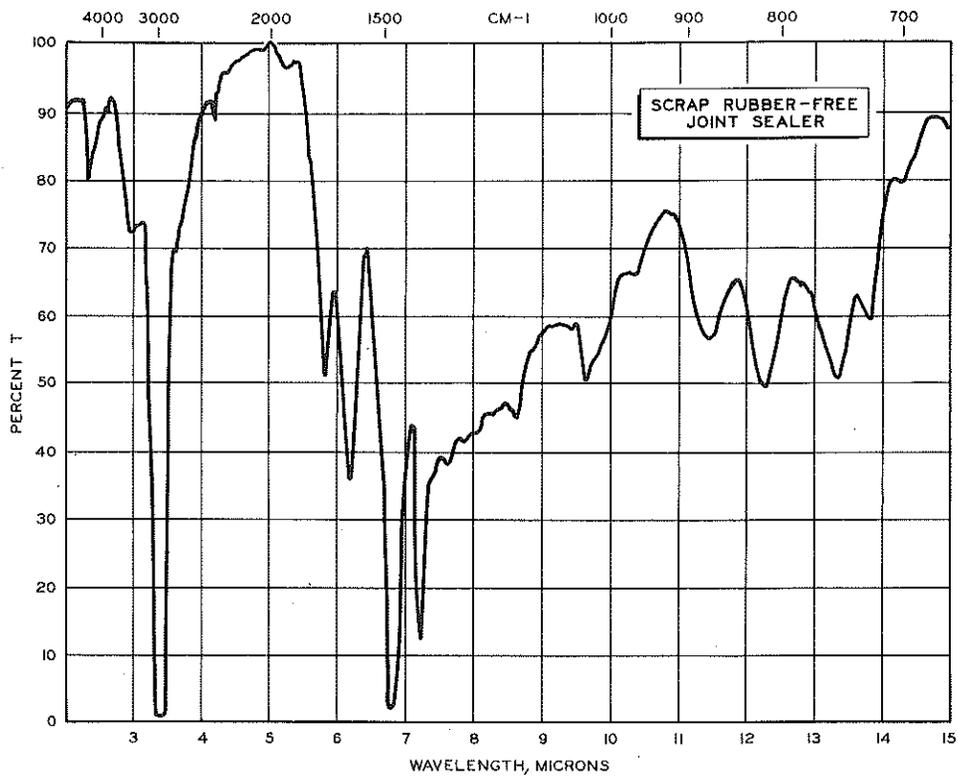


Figure 4. Infrared spectra of MEK extracts. The rubber scrap used was in the form of buffings from discarded tires.

Quantitative Infrared Studies

The possibility of determining the amount of cured rubber by using the intensity of infrared absorption at 10.3 microns was next investigated. Four samples of joint seal containing known amounts of cured rubber scrap were prepared by hot mixing and extracted with MEK. After removing the solvent, infrared spectra of the viscous liquid extracts were obtained using a 0.002-in. thick demountable cell. A plot of absorbance at 10.3 microns vs. scrap rubber content yielded the straight line calibration curve shown in Fig. 5. Joint sealers from four different manufacturers were then analyzed for scrap rubber by this infrared procedure. Table 2 shows typical results. Details of the experimental procedure appear in the appendix.

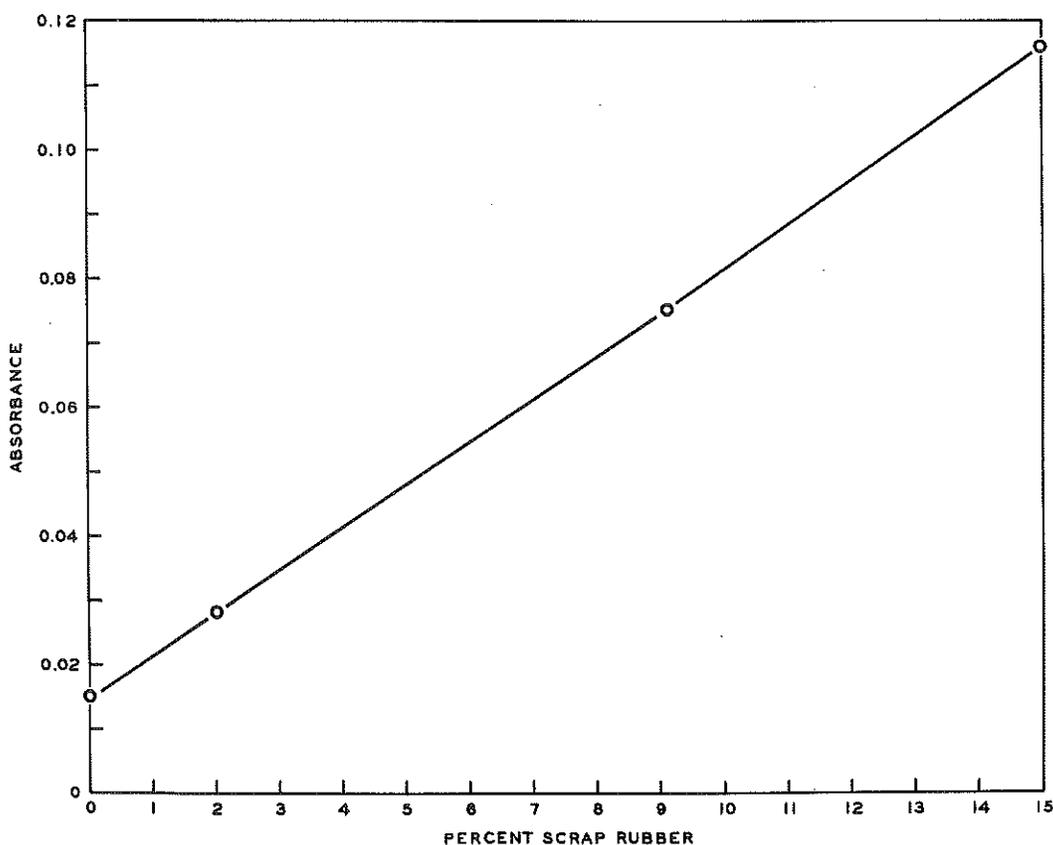


Figure 5. Calibration plot of absorbance at 10.3 microns vs. known cured rubber scrap content in hot-poured joint sealer.

The accuracy of the values obtained for cured rubber scrap content could not be estimated since no samples of scrap-free parent products were

available from the suppliers to run as blanks. The results are in agreement with verbal reports of industry practice, indicating that addition of 10 to 20 percent of cured rubber scrap to joint seal formulations is common.

TABLE 2
CURED RUBBER SCRAP CONTENT OF JOINT SEALERS

Sample	Percent MEK Solubles	Absorbance at 10.3 microns	Percent Cured Rubber Scrap
Reference	61.0	0.075	9.1*
A	52.7	0.085	9
B	72.6	0.074	11
C	69.9	0.077	11
D	71.2	0.081	12

* Calculated for a sample prepared by hot mixing known weights of cured rubber scrap and scrap-free joint sealer.

Note

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Bureau of Public Roads.

APPENDIX: EXPERIMENTAL PROCEDURE

A. Preparation of thin films of hot-poured joint sealer for microscopic examination. A 1.5 by 4 in. glass microscope slide is heated to approximately 150 C on an asbestos pad on a hot plate. Smear a thin strip of joint seal 1 by 0.25 in. onto the center of the slide with a small spatula. Spread a drop or two of mineral oil over the surface of the sealer. Place a thin layer of bonding agent (asphalt or a suitable joint seal) on the slide in a rectangle surrounding the sample, leaving 3/8-in. between materials. Cover the slide with a second slide and apply gentle pressure until the air is expelled and the mineral oil-joint sealer mixture flows into contact with the bonding agent. Remove the slide and asbestos pad from the hot plate as a unit and place on a flat surface. Pad the upper glass slide with a paper towel and apply approximately 13 lb of weight to the unit while it cools. The mounted specimen is then ready for microscopic examination.

B. Preparation of reference samples of joint seal containing ground, cured rubber scrap for use in plotting calibration curves. Weigh out a quantity of scrap-free joint seal in a suitable wide-mouth container. Calculate and weigh out the required quantity of ground, cured rubber scrap (tire buffings). Melt the joint seal over gentle heat on a hot plate or burner (maximum temperature: 380 F). Add the ground rubber scrap and stir thoroughly. Heat the mixture in an oven at 380 F for 20 min, cool in air, and store in a dust-free manner until used.

C. Infrared analysis for cured rubber scrap. Weight out three 1-g samples of joint seal into 250-ml beakers, add 75 ml of MEK, and stir. Cover the beaker with a watch glass and heat on a steam bath for 1 hr, stirring frequently to break up lumps. Allow the residue to settle and decant the liquid through a Gooch crucible fitted with a glass fiber filter paper (Reeve Angel and Co. No. 934AH). Some filter pulp may be added to the crucible to prevent clogging of the filter paper by fine particles. The filter should not be allowed to dry out during filtration. Wash the residue in the beaker with three 15-ml portions of warm solvent, decanted through the filter. Transfer the filtrate to a tared 250-ml beaker for evaporation of the solvent on a steam bath. Dry the residue in an oven at 100 C for 1 hr. Cool and reweigh the beaker to obtain the weight of soluble material. Calculate the fraction soluble in MEK.

A portion of the MEK soluble fraction is placed in a demountable cell using a 0.002-in. brass spacer. Use only enough sample to fill the cell and tighten the cell screws evenly to avoid cracking the sodium chloride windows. (When cleaning the cell, place the windows in chloroform and carefully slide them apart without damaging the spacer).

Set up the infrared spectrophotometer for quantitative work. The following conditions were used for a Perkin-Elmer Model 21 instrument:

Speed	3 min per micron
Response	1
Suppression	0
Pen Speed	3-sec. full scale
Slit Width, mechanical	246 microns
Source Current	0.3 amp

Place the demountable cell containing the sample in the sample beam, and a beam attenuator in the reference beam. Adjust the attenuator to obtain an absorbance reading of 0.150 for the sample at 9.0 microns. Scan slowly over the range 9 to 11 microns. Determine the absorbance of the absorption peak at 10.3 microns above a baseline drawn between the absorption minima at approximately 10.2 and 10.7 microns. Read the apparent scrap rubber content from the calibration curve and correct for variation in sample solubility as follows:

actual scrap rubber content =

$$\text{apparent scrap rubber content} \times \frac{\% \text{ MEK solubles of sample}}{\% \text{ MEK solubles of standard}}$$

REFERENCES

1. Information supplied by joint seal manufacturers.
2. Whitby, G. S., SYNTHETIC RUBBER, Wiley, New York, 1954.
p. 5.