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## A SIMPLIFIED METHOD FOR THE SEPARATION AND IDENTIFICATION OF HOT-MELT ADHESIVE COMPONENTS

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### SUMMARY

A simplified method was developed for the identification of all organic components in "hot-melt" adhesives. This method utilizes the principle of column chromatography to elute the different organic components, other than the base polymer and inorganic fillers, by using selective solvents. Infrared spectroscopy is used to identify all organic and inorganic components. However, emission spectroscopy was used to identify the inorganic fillers, when the infrared technique could not be used to achieve identification.

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### INTRODUCTION

Little has been published on the separation and identification of "hot-melt" (HM) adhesives. Recently, Finch and Kidman<sup>1</sup> presented a separation scheme based on a solvent extraction technique. Since HM adhesives can be formulated either using simple systems (*e.g.*, rubber and resin) or complex mixtures (*e.g.*, rubbers, resins, waxes, plasticizers and fillers), a general separation scheme will not necessarily work in all cases. Hence, other workers<sup>2-5</sup> have used a combination of techniques such as infrared (IR) spectroscopy, differential scanning calorimetry, colorimetric and chemical techniques to identify the components present in the HM.

In our studies, we have developed a simplified method for identification of the components in a HM adhesive. This method utilizes the principles of column chromatography to achieve the fractionations of all organic components, an automated fraction collector to isolate the fractions, and IR spectroscopy to identify the components. In cases where fillers are present, column chromatography cannot be used to achieve separation of the fillers. If IR techniques cannot be used to achieve identification, other techniques such as emission spectroscopy have been employed.

### EXPERIMENTAL

The HM adhesive is first cast as a thin film on a PTFE sheet, or if it is millable, it can be milled on a *cold* mill into a thin film. Five grams of the sheeted compound are accurately weighed, wrapped in a perforated PTFE film (about 0.005 in. thick), placed in an extraction thimble and Soxhlet extracted, usually for 16 h. Two solvents

found to be most efficient in connection with HM adhesive extractions are methyl alcohol and isopropyl alcohol. After extraction, the sample is dried in a vacuum oven at 50° until no change in weight results.

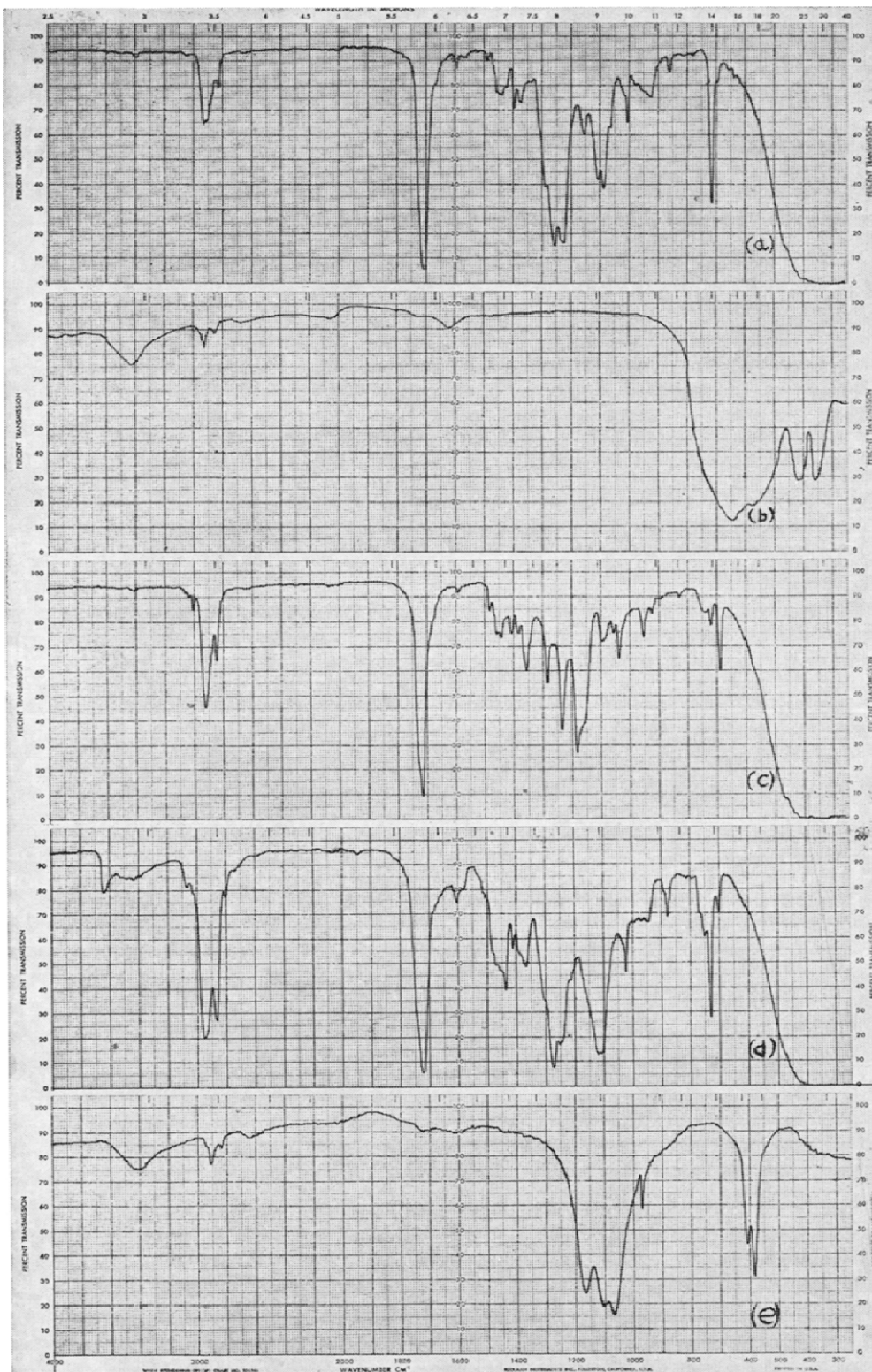
IR spectra are obtained on both the extracted compound and the alcohol extractables. These results help identify polymer type and in some cases other additives present (*e.g.*, plasticizers, resins, waxes, etc.). The ash content of the sheeted HM compound is obtained by ashing in a muffle furnace at 550° for 16 h (ref. 6). The ashing and solvent extractions are determined simultaneously to minimize time losses. The ash is analyzed by IR spectroscopy and by emission spectroscopy (if needed) to identify the type of filler present in the compound, if any.

The alcohol is completely removed from the organic extractables by evaporation prior to addition to a silica gel column. A 500-mm length glass column with 20 mm I.D. is fitted on one end with a PTFE stopcock containing a fritted glass support disc. About 400 mm of the column is filled with a slurry of silica gel in CCl<sub>4</sub> (Merck 7734 silica gel, 0.05–0.20 mm, 70–325 mesh ASTM). A known amount of the extractables is dissolved in hot CCl<sub>4</sub> and the CCl<sub>4</sub> solution cooled to room temperature before being added onto the column. Care should be taken in adding excess material or overloading of the column may result. As a guide for preventing overloading, the following is suggested: for a two-component system, the ratio of extractables to silica gel should be 0.1 g of extractables to every 10 g of silica gel; for systems containing two or more components, the ratio of extractables to silica gel should be 0.1 g to every 20 g. A 250-ml portion of each eluent is passed through the column at a constant flow-rate. The solvent eluents are introduced in the following sequence: carbon tetrachloride (CCl<sub>4</sub>); 50% CCl<sub>4</sub> + 50% benzene or toluene; benzene or toluene; 50% benzene or toluene + 50% chloroform; chloroform; 50% chloroform + 50% acetone; acetone; 50% acetone + 50% methanol; methanol. Every 10-ml fraction is collected either manually or using a fraction collector. All solvents used in this work were of spectroquality grade to avoid any contamination usually found in solvents other than spectrograde type. An IR spectrum is run on every fifth fraction so as to identify the component in this fraction. This is repeated until a new material shows up on the IR spectrum. When each fraction analyzed is different from the one preceding it, fractions in between are checked until the separation point is determined. All fractions of the same identification or same IR spectrum are combined and weighed to obtain quantitative results.

## RESULTS AND DISCUSSION

A typical HM adhesive might consist of a polymer (*i.e.*, a polyester, ethylene-vinylacetate), additives (*i.e.*, paraffin wax, hydrocarbon resins, plasticizers and antioxidant) and sometimes a filler (*i.e.*, titanium dioxide, barium sulfate). Alcohol extraction removes the organic additives in most cases, leaving behind the polymer and the filler, if present in the formulation. The latter could be determined by ashing<sup>6</sup> the sample and analyzing the ash by IR spectroscopy or by emission spectroscopy (if needed). Separation of the organic ingredients is accomplished using certain eluents.

Paraffin oils, chlorinated hydrocarbon resins, paraffin wax, and silicone oil are separated with the CCl<sub>4</sub> solvent. Most of the tackifying resins of the hydrocarbon



**Fig. 1. Infrared spectra. (a). Polyester; (b), titanium dioxide (Rutile); (c), styrenated polycaprolactone; (d), polyester; (e), barium sulfate (Barytes, Mineral).**

type (the aromatic as well as the aliphatic types) will separate with the benzene or the toluene phase, followed by separation of plasticizers in the chloroform phase. The acetone phase will separate the rosin acids and rosin esters, and finally the surfactants will separate with the methanol phase. Depending upon the antioxidant type, it can be separated in any of the above solvent phases. The total time of separation and identification of the components takes anywhere between 4 and 8 h, using both IR spectrophotometry and column chromatography. However, when a fraction collector is used, such as a Brinkmann Linear II Fraction Collector, the total time of analysis of one sample is reduced to about half the time used to run an analysis of this type. For the purpose of the quantitation of data, all samples of similar components are weighed as one component. A HM adhesive compound consisting of a polyester polymer, two organic additives and a filler (30% polyester (see Fig. 1d), 23% styrenated resin, 23% styrene-acrylonitrile-indene resin and 24% barium sulfate (Barytes, Mineral, see Fig. 1e)), was chosen to illustrate how a typical analysis was obtained. The sample was treated, prior to the alcohol extraction, in the manner described above in the experimental section. The HM compound was then extracted with isopropyl alcohol to remove the organic additives. Total percentage alcohol extractables amounted to 46%. The total alcohol extractables after evaporating the alcohol were dissolved in  $\text{CCl}_4$  and eluted through the silica gel column in the manner described above. A styrenated resin eluted with 50%  $\text{CCl}_4$  + 50% toluene and accounted for 23% by weight of the total HM adhesive compound. The IR spectrum of this component resembled that of the Sadtler<sup>7</sup> commercial IR spectrum D 1589. A styrene-acrylonitrile-indene resin eluted with 100% toluene solvent. It also accounted for 23% by weight of the total HM adhesive compound. The IR spectrum of this component resembled that of the Sadtler<sup>7</sup> commercial IR spectrum D 4211.

The total sample was ashed and the ash amounted to 24% in this particular sample. The IR spectrum of the ash was identified as that of barium sulfate, shown as Fig. 1e. From the knowledge of the percentages of additives and filler, the base polymer content was found to be 30%. IR analysis identified the base polymer as a polyester type (a new polyester type only recently introduced into the market), and is shown in Fig. 1d. The exact type of polymer in this HM adhesive was identified by reference to standard IR spectra<sup>7</sup>. This HM adhesive also served to illustrate the quantitative aspect of this method. Experimental results obtained showed no more than 1% by weight deviation of each organic additive, from the actual level present in the HM formulation. The deviation obtained usually can be due to loss upon evaporation of the solvent and possible adsorption of the material by the column support. During the course of this work we came across other base polymers for which no published IR spectra were available. The IR spectra of these polymers are also given in Fig. 1 as spectra (a) and (c). These polymers composed single component HM adhesive systems. The IR spectra shown in Fig. 1 (b) and (e) represent inorganic fillers most frequently found in HM adhesive formulations. They are obtained by ashing the total compound and running an IR spectrum on the ash using a KBr pellet technique. It should be noted that these inorganic materials cannot be separated by column chromatography, but can be easily identified using IR spectroscopy.

Other typical materials found in various HM adhesives from work of this type are styrene-isoprene-styrene block copolymer, styrene-butadiene-styrene block copolymer, ethylene-vinylacetate, atactic polypropylene, vinylpyrrolidone-vinyl-

acetate copolymer (in water sensitive HM adhesive), paraffin wax, polyterpene resin, wood rosin, coumarone-indene resin, polyester plasticizers, and 4,4'-methylene bis(2,6-di-*tert.*-butylphenol). The characterizations of these materials were very specific. In some cases, the HM formulations containing some of the above were very unique, especially when the end use was considered.

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