

## TECHNICAL NOTE

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### Solubility Characterization of Automotive Paints

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**ABSTRACT:** A solubility scheme is presented that will distinguish nonaqueous dispersion (NAD) lacquers, solvent-thinned lacquers, solvent-thinned enamels, and water-based enamels. This approach is suitable for milligram samples of evidence automotive paints.

**KEYWORDS:** forensic science, paint, solubility, automobiles

A scheme for the characterization of automotive finishes based on solubility tests has been previously described by this laboratory [1,2]. This technical note describes an extension of this scheme to permit the solvent-thinned acrylic lacquers to be distinguished in most instances from the nonaqueous dispersion (NAD) lacquers.

Acrylic lacquers are used for approximately 50% of all the automotive finish coats in the United States [3]. The basic resin is comprised of methyl methacrylate, although it may be modified by other methacrylic or acrylic monomers. The acrylic lacquers are applied in one of two forms: (1) solvent-thinned lacquers (also referred to as solution lacquers) and (2) NAD lacquers. The latter types have slightly higher molecular weights and some modification of the polymer to achieve partial solubility in aliphatic solvents when in the wet state.

Both types of lacquers are readily soluble in many organic solvents, including acetone and glacial acetic acid. The NAD acrylic enamels are soluble in xylene at room temperature, however, whereas the solvent-thinned acrylic enamels are not.

The acrylic enamels utilized as topcoats for automobiles are of three types: (1) solvent-thinned enamels (also referred to as organic dispersed enamels), (2) nonaqueous dispersions, and (3) water-based enamels. All three types are modified acrylic resins which contain some free acrylic and methacrylic acids as well as hydroxy containing monomers to facilitate cross-linking along the polymer chain. The cross-linking agent most commonly used is butylated melamine formaldehyde.

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The water-based acrylic enamels are based on polymers similar to those used in the organic dispersed enamels, except that the percentage of hydroxy containing monomers is reduced and the percentage of the free acids is increased. The cross-linking agent for these enamels, however, is hexamethoxymethyl melamine. The water-based enamels currently represent a small proportion of the total acrylic enamels used in automotive applications. Their use, however, is steadily increasing.

The types of chemical bonding involved in the cross-linked acrylic enamels are numerous. The principal bonding includes:

- (1) ester linkages between the methylol group of the melamine and the free acid in the acrylic chain, and the ester linkage of the hydroxy-alcohol in the acrylate;
- (2) ether linkages between the methylol group of the melamine and the free hydroxy groups incorporated in the acrylic polymer; and
- (3) alkylamine-type linkages between the melamine and the methylol groups.

Each of these represents candidate linkages to be chemically attacked and broken in order to characterize by solubility the otherwise insoluble polymer. The most sensitive bond to chemical attack is the ester bond. Bonds of this type are susceptible to hydrolytic attack by strong base, for example, alcoholic potassium hydroxide. The alkylamine linkages may be broken by Hoffmann degradation. This degradation is carried out by exhaustive methylation of the amine with methyl iodide, oxidizing the product with hydrogen peroxide, and then pyrolyzing the product. Because of the complexities of this latter approach and the difficulties in standardization of techniques, the former approach was used. Hot saturated ethanolic potassium hydroxide was found to be suitable for breaking the ester bonds. However, the solution must be freshly prepared; otherwise the results are not entirely reproducible. A saturated solution of potassium hydroxide in tertiary-butanol was found to be a more suitable reagent for the enamels; this reagent need not be freshly prepared.

The water-based enamels are not dissolved by hot alcoholic potassium hydroxide unless they are first treated with a strong acid. A short treatment with hot concentrated nitric acid provides a sufficient induction for a subsequent attack with alcoholic potassium hydroxide.

The full solubility protocol is diagrammed in Fig. 1. A small amount of paint is placed in a white porcelain spot plate. A few millilitres of xylene (CAUTION: TOXIC) at room temperature are added. At this point the NAD acrylic lacquers will dissolve. If the paint does not dissolve, the xylene is removed by blotting and a few millilitres of glacial acetic acid at room temperature are added. If the paint is a solvent-thinned acrylic lacquer, it will dissolve within 2 min. If the paint does not dissolve in the glacial acetic acid, the spot plate is heated with an infrared lamp placed approximately 20 to 25 cm from the plate. When the temperature is within 10° of the boiling point of glacial acetic acid (117°C), the paint will dissolve within 2 min if the paint is an organic-dispersed (solvent-thinned) acrylic enamel. If no reaction occurs, remove the acetic acid by either a pipet or by continued evaporation and add a few drops of concentrated nitric acid and reheat for 3 min. The function of the nitric acid at this point is to break the cross-linkages, and solubility of the paint is not to be expected at this stage. The sample is then rinsed with distilled water and blotted dry. A few millilitres of a saturated solution of potassium hydroxide in tertiary-butanol is then added to the spot plate and the solution is heated as before with the infrared lamp. The water-dispersed acrylic enamels will now dissolve within 2 to 3 min.

The method described works well in the overwhelming majority of cases. It should be recognized, however, that small variations in plasticizer, cellulosic type modifications, acrylic polymer composition, and molecular weight may affect in subtle ways the solubility properties of a paint; this is perhaps more so in the case of the acrylic lacquers than the enamels. The significance of this is that occasional aberrances in any solubility scheme are to be expected. In performing the solubility tests described above on the 1977 National Bureau

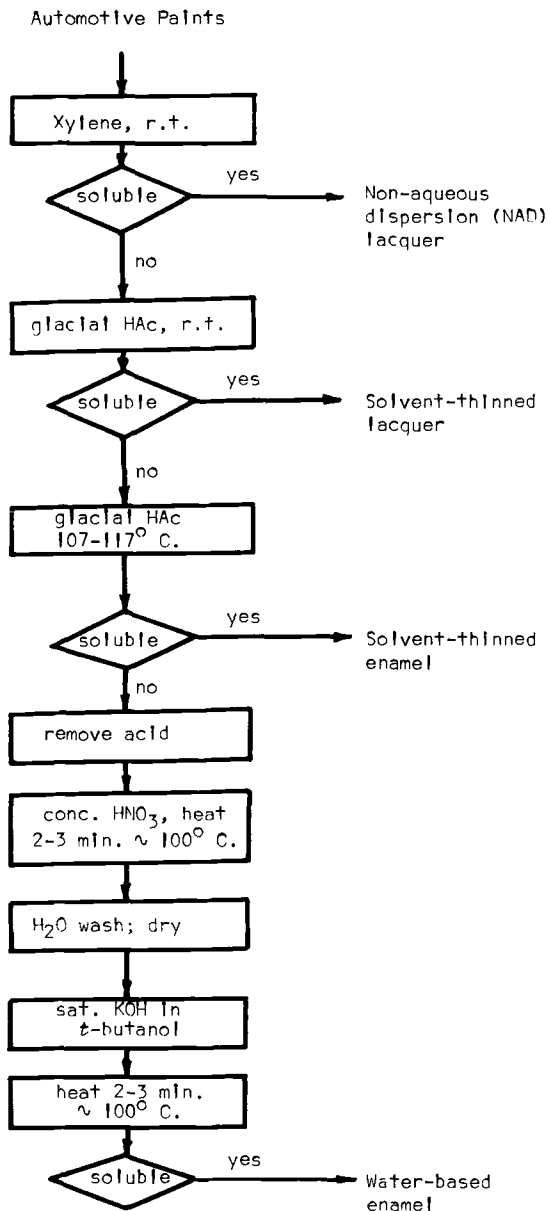


FIG. 1—Solubility scheme for the characterization of acrylic automotive paints.

of Standards automotive paint samples, two aberrances were noted. Samples DB77F0339 and DB77B0272, ostensibly NAD lacquers, failed to dissolve in xylene as expected.

**References**

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