

**NBS Special
Publication
480-40**

Paint Solubility Testing

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A11106 312895

**NBS
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**Law Enforcement
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**U.S. DEPARTMENT OF
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National Bureau of
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No. 480-40
1982
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ACKNOWLEDGMENTS

This report was prepared by the Law Enforcement Standards Laboratory of the National Bureau of Standards under the direction of Paul H. Krupenie and Lawrence K. Eliason, Chief of LESL. The preparation of this report was sponsored by the National Institute of Justice, Lester D. Shubin, Standards Program Manager.

Paint Solubility Testing

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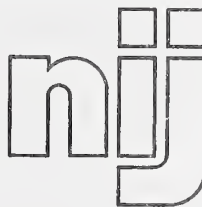
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National Institute of Justice
U.S. Department of Justice
Washington, DC 20531



Issued
January 1982

U.S. DEPARTMENT OF COMMERCE
Malcolm Baldrige, Secretary

NATIONAL BUREAU OF STANDARDS
Ernest Ambler, Director

National Bureau of Standards
Special Publication 480-40

SECT 1 RAM

Library of Congress Catalog Card Number: 81-600176

National Bureau of Standards
Special Publication 480-40
Nat. Bur. Stand. (U.S.), Spec. Publ. 480-40, 20 pages
CODEN: XNBSAV

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1982

Available from the National Technical Information
Service, Springfield, VA 22161.

FOREWORD

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Technical comments and suggestions concerning this report are invited from all interested parties. They may be addressed to the Law Enforcement Standards Laboratory, National Bureau of Standards, Washington, DC 20234.

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PAINT SOLUBILITY TESTING

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This report presents the results of a study to develop criteria for the characterization of paint through solubility testing. Experiments were conducted with common solvents to classify chemical reactivity with automobile and household paints. Seven categories of reactivity are defined, which form the basis for specifying the extent of solubility of paints in various reagents under controlled conditions of time and temperature. The report also describes a novel solubility test procedure by which acrylic lacquers, organic-dispersed enamels, and water-based enamels can be distinguished through sequential testing, a characterization not previously accomplished with solubility testing.

Key words: automotive paints; household paints; sequential tests; solubility tests.

1. INTRODUCTION

The Nationwide Crime Laboratory Proficiency Testing Project conducted by the Law Enforcement Assistance Administration and the Forensic Sciences Foundation demonstrated a need for standardization in paint solubility testing for forensic purposes.¹ Based on results obtained for tests of several paint samples distributed to crime laboratories throughout the country, it was apparent that there was little or no standardization in the solubility test methods used, reproducibility of test results, and criteria for the evaluation and reporting of results, or, for that matter, in the rationale behind the use of a particular array of solvents. For example, one laboratory would report that a given paint sample was soluble in sulfuric acid, while another laboratory would report that the paint was insoluble in this reagent. Reagent concentrations and times of reaction were frequently not reported. It was apparent that there was large variation in the reagents used, in the time allowed for the reagent to act on the paint, in the temperature at which the tests were conducted, and in the criteria applied to the term "soluble."

The purpose of the present study was to develop criteria to apply to solubility testing and chemical reactivity of automotive paints, and to standardize reagent concentration and other parameters. The principal focus of the study was testing acrylic enamels used as automotive finishes, since prior to this study these paints were reported to be virtually unreactive to all solvents when subjected to solubility tests. An ancillary objective was to apply these criteria of solubility and reactivity to testing household paints.

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¹ Crime Laboratory Proficiency Testing Research Program. Joseph L. Peterson, Ellen L. Fabricant, Kenneth S. Field, and John I. Thornton. Law Enforcement Assistance Administration, U.S. Government Printing Office, Washington, DC. Oct. 1978, 287 pp.

A. Sample Sources and Preparation

Samples of vinyl, alkyd, acrylic, and epoxy paints were obtained from retail distributors in Virginia, because State law requires all components of a paint to be indicated on the label, facilitating a confirmation of the generic type of paint. The samples tested were specifically designated as exterior grade paint. The vinyl and acrylic paints were water-based and the alkyd and epoxy paints were oil-based. The epoxy was cross-linked. The paints were selected to be deeply pigmented, i.e., highly saturated with pigment, to permit a more critical assessment of solubility and/or pigment leach. Linseed oil paint, as an example of an air-oxidizing drying oil paint, is rarely marketed now; the linseed oil paint used in this study was made by adding pigment (25% by weight of rutile titanium dioxide) to commercially available dark boiled linseed oil by stirring. No thinners were used; but dark boiled linseed oil contains a drier. The household paints were brushed as thin [approximately 3 mil (.075 mm)] films onto a sheet acetate substrate and permitted to fully cure at room temperature for a minimum of 5 weeks before testing. No primers were used with any of the household paints.

The automobile paints tested were the separate chemical samples from the 1977 National Bureau of Standards' "Reference Collection of Automotive Paints."² These automotive paints consisted of acrylic lacquers and acrylic enamels as defined by Williams.³ Acrylic enamels were of three types: (1) organic dispersed enamels, also referred to as "solvent-thinned" enamels, (2) non-aqueous dispersion enamels, and (3) water-based enamels. The term water-based enamel is used interchangeably with water dispersion enamel or aqueous dispersion enamel.

B. Reagents

A wide range of solvents and chemical reagents were tested for their efficacy in dissolving both household and automotive paints. These included acids, bases, and organic solvents covering a wide range of polarity. Particular attention was given to reagents reported in the Crime Laboratory Proficiency Project report as having applicability to paint solubility testing.

All chemicals were of analytical reagent grade. Dilutions, whether of a liquid stock solution or of a stock solid, are expressed as a weight to weight (w/w) percentage.

Stock Acids:

Acetic Acid, CH_3COOH , glacial (17.4 M)

Hydrochloric Acid, HCl , conc. (11.6 M)

Nitric Acid, HNO_3 , conc. (15.4 M)

Phosphoric Acid, H_3PO_4 , conc. (14.6 M)

Sulfuric Acid, H_2SO_4 , conc. (18.0 M)

Stock Bases:

Ammonium Hydroxide, NH_4OH , conc. (14.8 M)

Potassium Hydroxide, KOH , 95 percent sticks

Sodium Hydroxide, NaOH , 95 percent sticks

² 1977 Reference Collection of Automotive Paints, National Bureau of Standards and Manufacturers Council on Color and Appearance, Inc.

³ *Automotive Finishes*. Ralph A. Williams, Federation Series on Coatings Technology, Federation of Societies for Paint Technology, 121 South Broad St., Philadelphia, PA 19107, 1977, 36 pp.

Organic Solvents:

Acetone, b.p. 56 °C
Amyl Acetate, b.p. 149°
Benzene, b.p. 80°
t-Butanol, b.p. 82°
Carbon Disulfide, b.p. 46°
Carbon Tetrachloride, b.p. 76°
Chloroform, b.p. 61°
Dichloroethane, b.p. 57°
Dichloromethane, b.p. 40°
Dimethylformamide (DMF), b.p. 149-156°
Dimethylsulfoxide (DMSO), b.p. 189°
p-Dioxane, b.p. 101°
Ethanol, absolute, b.p. 78°
Ethyl Acetate, b.p. 77°
Methanol, absolute, b.p. 65°
Petroleum Ether, b.p. 60-80°
Piperidine, b.p. 106°
Tetrahydrofuran (THF), b.p. 64°
Toluene, b.p. 110°
Xylene (*o*-, *m*-, and *p*-isomers), b.p. 135-140°

C.(1) Experimental, Household Paints

The effect of each solvent on each sample of paint was evaluated at room temperature (23 °C) and, for most solvents, at elevated temperatures. The high volatility of certain solvents (e.g., carbon disulfide and acetone) presented serious practical difficulties in solubility testing at elevated temperatures. Refluxing would have addressed this problem, but it was concluded that this would not be practical for routine use in forensic laboratories and that standardization of refluxing procedures would create further problems.

Tests at all temperatures were observed under a low-power stereoscopic binocular microscope. Tests at room temperature were conducted in a white porcelain spot tile. The tests at elevated temperature were conducted in tubes immersed in a water bath heated to a temperature determined by the boiling point of the reagent. The temperature selected was close to the boiling point, but not so close that the vapor pressure at the selected temperature would result in an excessively rapid evaporation of the solvent. The tubes and reagents were preconditioned to the temperature of the water bath prior to the addition of the paint samples.

At all temperatures, the ratio of reagent to sample was greater than 50:1 by weight. Samples of paint approximately 1 mm × 1 mm were removed from their acetate substrate and immersed in the reagent for a period of 5 min. The reagents containing the samples were stirred at intervals of 1 min. Various reaction times were tried, but the 5-min reaction time was the most suitable; exposure times up to several hours did not alter the chemical reactivity assessed at 5 min. Solubility or other chemical reactivity was assessed by the following criteria:

Soluble A sample was determined to be soluble if the paint was completely disintegrated within 5 min, either as a result of solvation or chemical decomposition.

Partially soluble A sample was determined to be partially soluble if after 5 min a significant amount of pigment (more than half) was leached from the paint with some, although incomplete, disintegration of the vehicle.

Pigment leach A sample was determined to have undergone pigment leach if the paint remained substantially intact after 5 min, but with some pigment (less than half) extracted by the reagent. Pigment leach is distinguished from "partially soluble" in that the paint remains substantially intact and exhibits little or no visual evidence of disintegration of the vehicle.

Swell A sample was said to swell if there was a significant and uniform expansion of the paint, but with no noticeable solubility or pigment leach.

Curl A sample was said to curl if there was a tendency for the paint to curl in the reagent, but with no noticeable solubility or pigment leach. Curling is probably an asymmetrical form of swelling.

Discolor A sample was said to discolor if the paint turned brown or black. This phenomenon was noted with the mineral acids, and represents a charring of the organic matter. Care must be exercised when dealing with black or brown paints that true solvation not be confused with discoloration; although arising from different chemical considerations, the subjective appearances would be quite similar.

Soften A sample was said to soften if, after exposure to the solvent, the paint fragment could be penetrated with a needle but was otherwise not visibly affected.

C.(2) Experimental, Automotive Paints

In the case of the sequential solvent testing of automotive paints, the tests were conducted in a white porcelain spot tile. Heating, where needed, was with a 500-W infrared lamp 15 cm from the tile. Tests were observed under a low-power stereoscopic binocular microscope. Paint samples approximately 1 mm × 1 mm were removed from their metal substrate and placed in the spot plate. Glacial acetic acid at room temperature was added. If the paint was an acrylic lacquer, it would dissolve within 2 min. If the paint did not dissolve, the spot plate was heated with the infrared lamp. When the temperature was within 10 °C of the boiling point of glacial acetic acid (117 °C), the paint would dissolve within 2 min if the paint were an organic-dispersed enamel.

At a distance of 15 cm from the 500-W lamp a steady state situation was achieved with respect to temperature; the heat input was equal to the heat loss, and the temperature remained essentially constant at approximately 107–110 °C. If no reaction occurred under heating, the acetic acid was removed by means of a pipette, a few drops of concentrated HNO₃ was added, and the sample was reheated with the infrared lamp for an additional 3 min. The paint sample was then washed in distilled water and dried. This was accomplished *in situ* by drawing off the acid with a pipette, adding water, drawing off the water with a pipette, repeating the washing step, and drying the sample by heat from the infrared lamp. A saturated solution of potassium hydroxide in tertiary butanol was then added, and the solution was heated by means of the infrared lamp. The water-based enamels then dissolved.

3. RESULTS AND DISCUSSION

A. General

Both household and automotive paints vary within a particular generic type. This variation in composition (e.g., the substitution of a methoxy group into a resin monomer) results in some variation in solubility behavior. For example, within the acrylic enamel group, hot nitric acid will only discolor one paint sample, but will completely dissolve other samples. As a consequence, the use of solubility testing to individualize a paint or to definitively characterize an evidence paint as belonging to a particular generic type should be attempted only with caution. The principal application of paint solubility testing is in screening or comparison.

Certain generalizations, however, may be made. For household paints, the most effective solvents are concentrated H₂SO₄, 30 percent (w/w) KOH, and hot HCl. These reagents will result in either a dissolution of the paint or in a color reaction which may have some diagnostic value.

For automotive paints, acetone, phosphoric acid, and dimethylformamide are well suited to dissolve the acrylic lacquers. The acrylic enamels are much more resistant to the effects of solvents in general, but the strong mineral acids may achieve some reactivity. The failure of the acrylic enamels to dissolve in most common reagents led to the sequential testing which was the principal thrust of this study. Because of their significance the findings will be discussed in a separate section.

B. Household Paints—General Solubility

The results of the solubility testing of the household paints at room temperature and at elevated temperatures are in tables 1A through 1E, 2A through 2E, and 7. Non-polar solvents have very little effect in dissolving household paints. If a solvent had little or no effect on any paint at any temperature up to and including the boiling temperature, it will not appear in any of the tabular data except to indicate the comprehensiveness of the testing conducted, i.e., to indicate the logical candidate solvents within a particular group.

TABLE 1A. *Household paints at room temperature, concentrated acids*

Paint	Acid			
	H ₂ SO ₄ (conc.)	HCl (conc.)	HNO ₃ (conc.)	HAc (glacial)
Vinyls	Soluble	No reaction	Softens; may discolor	Softens
Alkyds	Curls; may discolor	No reaction	Curls; may discolor	Curls
Acrylics	Soluble	No reaction	Softens	Softens
Linseed oil base	Soluble; may discolor	No reaction	Discolors	No reaction

TABLE 1B. *Household paints at room temperature, strong bases*

Paint	Base				
	NaOH (30%, w/w)	KOH (30%, w/w)	NH ₄ OH (conc.)	KOH (1%, w/w)	NaOH (50%, w/w)
Vinyls	No reaction	No reaction	No reaction	No reaction	No reaction
Alkyds	No reaction	Soluble	Curls; may discolor	No reaction	No reaction
Acrylics	No reaction	No reaction	No reaction	No reaction	No reaction
Linseed oil base	Soluble	Soluble	No reaction	Softens	No reaction

TABLE 1C. *Household paints at room temperature, non-polar solvents*

Paint	Solvent				
	C_6H_6	CS_2	CCl_4	Dioxane	Pet. Ether
Vinyls	No reaction	No reaction	No reaction	No reaction	No reaction
Alkyds	No reaction	No reaction	No reaction	No reaction, or may soften	No reaction
Acrylics	Softens	No reaction	Softens	Softens	No reaction
Linseed oil base	No reaction	No reaction	No reaction	Softens	Swells

TABLE 1D. *Household paints at room temperature, low to medium polarity (dielectric constant <6) solvents*

Paint	Solvent			
	Toluene	Xylene	Amyl acetate	$CHCl_3$
Vinyls	No reaction	Softens	Softens	Softens
Alkyds	No reaction	No reaction	Softens	No reaction
Acrylics	Softens	Softens	Softens	Softens
Linseed oil base	No reaction	No reaction	Softens	No reaction

TABLE 1E. Household paints at room temperature, medium to high polarity (dielectric constant >6) solvents

Paint	Solvent								
	THF	Ethanol	Methanol	Ethyl Acetate	CH ₂ Cl ₂	Acetone	DMF	DMSO	Piperidine
Vinyls	No reaction	No reaction	No reaction	No reaction	No reaction	Softens	Softens	No reaction	Softens
Alkyds	No reaction	No reaction	No reaction	No reaction	Curled; may swell	No reaction	Softens	No reaction	Softens; swells
Acrylics	No reaction	No reaction	No reaction	No reaction	Softens	Softens	Swells	No reaction	Softens
Linseed oil base	No reaction	No reaction	No reaction	Softens	No reaction	Curled	Softens	Softens	Softens
									Swells

TABLE 2A. Household paints at $80\pm5^\circ\text{C}$, concentrated acids

Paint	Acid			
	H ₂ SO ₄ (conc.)	HCl (conc.)	HNO ₃ (conc.)	HAc (glacial)
Vinyls	Soluble	Discolors	Softens; pigment leach	Softens
Alkyds	Soluble	No reaction	Discolors	No reaction
Acrylics	Soluble	Soluble	Soluble	Softens
Linseed oil base	Soluble; discolors	Discolors	Soluble; discolors	No reaction

TABLE 2B. Household paints at elevated temperatures, strong bases

Paint	Base			
	30% NaOH; 80 °C	30% KOH; 80 °C	1% KOH; 95 °C	50% NaOH; 95 °C
Vinyls	No reaction	No reaction	No reaction	No reaction
Alkyds	Discolors	Soluble	Soluble	Discolors
Acrylics	No reaction	No reaction	No reaction	No reaction
Linseed oil base	Soluble	Discolors; partially soluble	Discolors	No reaction

TABLE 2C. Household paints at elevated temperatures, non-polar solvents

Paint	Solvent		
	C ₆ H ₆ , 60 °C	CCl ₄ , 60 °C	Dioxane, 95 °C
Vinyls	Softens	No reaction	Swells
Alkyds	No reaction	No reaction	Softens
Acrylics	Swells	Swells	Softens
Linseed oil base	No reaction	No reaction	No reaction

TABLE 2D. Household paints at elevated temperatures, low to medium polarity (dielectric constant <6) solvents

Paint	Solvent			
	Toluene, 80 °C	Xylene, 95 °C	Amyl acetate, 95 °C	CHCl ₃ , 60 °C
Vinyls	No reaction	Pigment leach	Softens	Softens
Alkyds	Softens; discolors	Softens	No reaction	No reaction
Acrylics	Curls	Curls	Softens	Softens
Linseed oil base	No reaction	No reaction	Curls	No reaction

TABLE 2E. Household paints at elevated temperatures, medium to high polarity (dielectric constant >6) solvents

Paint	Solvent					
	Ethanol, 60 °C	Methanol, 60 °C	Ethyl acetate, 65 °C	Piperidine, 95 °C	DMF, 100 °C	DMSO, 100 °C
Vinyls	No reaction	Softens	No reaction	Softens	Softens	Softens
Alkyds	No reaction	No reaction	No reaction	Softens	Pigment leach	Softens; pigment leach
Acrylics	Softens	Softens	No reaction	Softens	Softens	Softens
Linseed oil base	Curls	Curls	Curls	Soluble	Curls	Softens

C. Automotive Paints—General Solubility

All acrylic lacquers dissolved in room-temperature glacial acetic acid. No acrylic enamel dissolved in this acid, even at high temperature. The results of solubility testing of acrylic lacquers at room temperature and at elevated temperatures are in tables 3A through 4B. Historically, these paints have not presented any problem with solubility testing, and a number of solvents are quite efficient in dissolving these paints and distinguishing them from the acrylic enamels. The results of solubility testing of acrylic enamels at room temperature and at elevated temperatures are in tables 5A through table 6. The aqueous dispersion enamels are poorly represented in the NBS 1977 Reference Collection of Automotive Paints, owing to their recent introduction; the reactions of a single paint of this type are presented in table 6.

TABLE 3A. *Automotive paints: acrylic lacquers at room temperature, strong acids*

Paint	Solvent			
	H ₂ SO ₄ (conc.)	HNO ₃ (conc.)	H ₃ PO ₄ (conc.)	HCl (conc.)
Acrylic solution lacquer				
DA77G0333	Soluble	Pigment leach	No reaction	No reaction
NA77B0334	Partially soluble	Partially soluble, discolors	No reaction	No reaction
PA77L0335	Soluble	No reaction	Discolors	Discolors
Acrylic dispersion lacquer				
DB77B0334	Partially soluble	Partially soluble, discolors	Discolors	Discolors

TABLE 3B. *Automotive paints: acrylic lacquers at 80 °C, strong acids*

Paint	Solvent			
	H ₂ SO ₄ (conc.)	HNO ₃ (conc.)	H ₃ PO ₄ (conc.)	HCl (conc.)
Acrylic solution lacquer				
DA77G0333	Soluble	Pigment leach	Discolors	Pigment leach
NA77B0334	Soluble	Partially soluble, discolors	Partially soluble	No reaction
PA77L0335	Soluble	Softens	Partially soluble	No reaction
Acrylic dispersion lacquer				
DB77B0334	Soluble	Partially soluble, discolors	Partially soluble, discolors	Discolors

TABLE 4A. *Automotive paints: acrylic lacquers at room temperature, miscellaneous solvents*

Paint	Solvent		
	Acetone	DMF	30% NaOH (w/w)
Acrylic solution lacquer			
DA77G0333	Soluble	Soluble	No reaction
NA77B0334	Soluble	Soluble	No reaction
PA77L0335	Soluble	Soluble	No reaction
Acrylic dispersion lacquer			
DB77B0334	Soluble	Soluble	No reaction

TABLE 4B. *Automotive paints: acrylic lacquers at elevated temperature, miscellaneous solvents*

Paint	Solvent	
	DMF, 80 °C	30% NaOH (w/w), 80 °C
Acrylic solution lacquer		
DA77G0333	Soluble	No reaction
NA77B0334	Soluble	No reaction
PA77L0335	Soluble	No reaction
Acrylic dispersion lacquer		
DB77B0334	Soluble	No reaction

TABLE 5A. Automotive paints: acrylic enamels at room temperature, strong acids

Paint	Solvent			
	H ₂ SO ₄ (conc.)	HNO ₃ (conc.)	H ₃ PO ₄ (conc.)	HCl (conc.)
Solvent-thinned (organic dispersed) acrylic enamel				
DC77F0339	Discolors	Pigment leach	Curls	Pigment leach, discolors
FC77C0090	Curls	Curls	No reaction	No reaction
LC77E0235	Pigment leach, discolors	Pigment leach, discolors	No reaction	No reaction
NC77B0308	No reaction	No reaction	No reaction	No reaction
PC77J0255	Discolors	Pigment leach	No reaction	Discolors
Non-aqueous dispersion enamel				
AN77H0313	Discolors	No reaction	No reaction	No reaction
BN77E0222	Discolors	Pigment leach	No reaction	No reaction
CN77A0123	Discolors	No reaction	No reaction	No reaction
FN77E0222	Discolors	Pigment leach, curls	No reaction	No reaction
KN77C0090	No reaction	No reaction	No reaction	No reaction
LN77B0149	Discolors	No reaction	No reaction	No reaction
NN77B0092	Discolors	Discolors	Discolors	Discolors
PN77F0314	Discolors	Pigment leach	No reaction	Discolors

TABLE 5B. *Automotive paints: acrylic enamels at $80 \pm 5^\circ \text{C}$, strong acids*

Paint	Solvent			
	H ₂ SO ₄ (conc.)	HNO ₃ (conc.)	H ₃ PO ₄ (conc.)	HCl (conc.)
Solvent-thinned (organic dispersed) acrylic enamel				
DC77F0339	Discolors	Soluble	Curls	Discolors, pigment leach
FC77C0090	Soluble	Soluble	No reaction	No reaction
LC77E0235	Discolors	Soluble	No reaction	No reaction
NC77B0308	Discolors	Discolors	Softens	Discolors
PC77J0255	Discolors	Soluble	Soluble	Discolors
Non-aqueous dispersion enamel				
AN77H0313	Discolors	Partially soluble	Soluble	Discolors
BN77E0222	Discolors	Partially soluble	No reaction	No reaction
CN77A0123	Soluble	Partially soluble	No reaction	No reaction
FN77E0222	Discolors	Partially soluble	No reaction	No reaction
KN77C0090	Discolors	Soluble	No reaction	Softens
LN77B0149	Discolors	Soluble	No reaction	No reaction
NN77B0092	Discolors	Soluble	Partially soluble	Softens
PN77F0314	Discolors	Soluble	Soluble	Discolors

TABLE 6. *Aqueous dispersion enamel (NBS #NW77E0054)—temperature as noted*

Solvent	Temperature	
	Room temperature	80 °C
H ₂ SO ₄ (conc.)	Curls, pigment leach	Solution yellows
HNO ₃ (conc.)	Curls, pigment leach	Soluble
H ₃ PO ₄ (conc.)	No reaction	Pigment leach
HCl (conc.)	No reaction	Pigment leach
NaOH (30%)	No reaction	No reaction
DMF	No reaction	Solution turns green
Acetone*	No reaction	NA

*Room temperature only; B. P. of acetone is 56.5 °C.

TABLE 7. *Epoxy paint—temperature as noted*

Solvent	Temperature	
	Room temperature	80 °C
H ₂ SO ₄ (conc.)	Softens, browns	Soluble
HNO ₃ (conc.)	No reaction	No reaction
H ₃ PO ₄ (conc.)	No reaction	No reaction
HCl (conc.)	No reaction	No reaction
NaOH (30%)	No reaction	No reaction
DMF	No reaction	No reaction
Acetone*	No reaction	NA

*Room temperature only; B. P. of acetone is 56.5 °C.

D. Automotive Paints—Sequential Solubility Scheme

The study of solubility characteristics of household paints follows the usual use of an array of solvents to assess the responses, e.g., the degree of solubility encountered. Topcoats for automobiles, by contrast, in many instances, were found to require a sequential testing scheme. To better express the rationale for this scheme, background information is presented on the chemical bond types that are to be broken in solubilizing such paints. Automobiles manufactured in the United States in recent years have been finished with acrylic topcoats.⁴ The acrylic resins may be in either a straight-chain thermoplastic as in the acrylic lacquers, or in a cross-linked thermoset form as in the acrylic enamels.

⁴ Williams, *op cit.*

The sequential solvent testing of automotive paints was derived from a review of the chemistry of automotive enamels by one of the authors (SK). This suggested that first it would be necessary to break the structural cross-linkages, followed by use of a reagent which would cause further dissolution of the partially-degraded polymer.

Acrylic lacquers are utilized for approximately 50 percent of all the automobile topcoat production in the United States. The basic resin is comprised of methyl methacrylate, which is modified by other methacrylic or acrylic monomers. The acrylic lacquers are applied in one of two forms: (1) solvent-thinned lacquers⁵ and (2) non-aqueous dispersion (NAD) lacquers.⁶ The latter types have slightly higher molecular weight polymers which are modified to achieve partial solubility in aliphatic solvents. Both types are readily soluble in many organic solvents, and there is no difference between the two types in the solubility characteristics of the paints after drying.

The acrylic enamels utilized as topcoats for automobiles are of three types: (1) solvent-thinned enamels, also referred to as organic dispersed enamels, (2) non-aqueous dispersions, and (3) water-based enamels.⁷ All three types are modified acrylic resins containing acrylic and methacrylic acids as well as hydroxy-containing monomers. The carboxyl and hydroxyl groups provide reactive sites for the crosslinking between polymer chains. The cross-linking agent most commonly used is butylated melamine formaldehyde.

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 is hexamethoxy-methyl melamine. The water-based enamels, at the present time, represent a small portion of the total amount of acrylic enamels used in automotive applications. Their use has been stimulated by antipollution regulations, however, particularly on the West Coast, and their use is likely to increase in the future.

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

- 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 into the acrylic polymer.
- 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 solubilize 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, e.g., ethanolic KOH. The alkylamine linkages may be broken by Hoffmann degradation. This degradation is carried out by exhaustive methylation of the amine with methyl iodide, oxidation of the product with hydrogen peroxide, followed by pyrolysis of the product. Because of the complexities of this latter approach, the former approach was first attempted. With a slight modification (substitution of tertiary-butanol), this method was applied successfully.

Saturated ethanolic KOH in the temperature range of 80–100 °C was found to be suitable for hydrolyzing the ester bonds. However, the solution must be freshly prepared or the results are not entirely reproducible. A saturated solution of KOH 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 KOH unless they are first treated with a strong acid. A pretreatment with hot conc. nitric acid chemically modifies the polymer to the extent that it becomes soluble in hot alcoholic KOH.

⁵ Solvent-thinned lacquers are also referred to as acrylic solution or organic dispersed lacquers.

⁶ NAD lacquers are also referred to as acrylic dispersion lacquers.

⁷ Williams, op cit.

4. CONCLUSIONS

Prior to this study, attempts to use solvents to characterize paint consisted of one-step tests, i.e., if a solvent failed to dissolve or react with a paint sample, it was discarded and another reagent was tried. This approach is sufficient to characterize the solubility reaction of reagents with household paints. The use of one reagent as an activator, with another solvent used in tandem on the same sample, is a novel approach. The present work describes a method wherein acrylic lacquers, organic-dispersed enamels, and water-based enamels can be distinguished by sequential tests. The method is outlined in figure 1. Primers do not interfere with this procedure. This represents a substantial breakthrough in the use of solubility testing for the characterization of automotive paints.

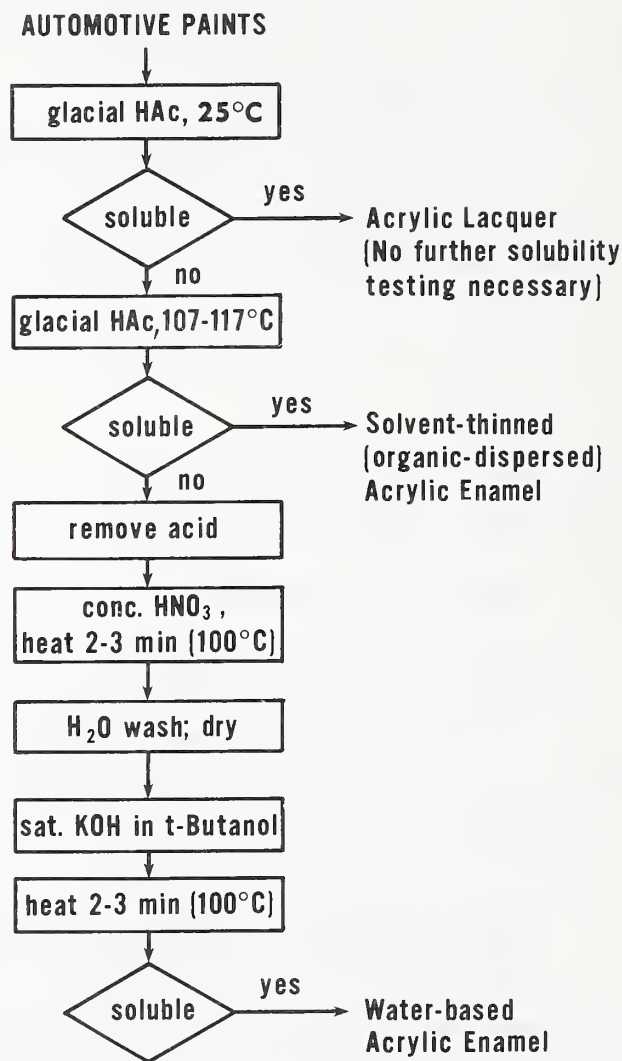


FIGURE 1. Solubility scheme for automotive paints.

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