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TECHNICAL NOTE

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Application of the Le Rosen Test to Paint Analysis

Reliable, discriminating spot tests can be important in rapidly determining differences involving paint sample comparisons. Reagents offering high color intensity with a broad-ranged spectrum obviously produce the best basis for sample analysis. The Le Rosen reaction [*1*, pp. 137–140] is such a test, offering definitive discrimination of many aromatic compounds. Application of this test to small paint samples offers a clearer differentiation than sulfuric acid [*2*] and a wider applicability than diphenylamine-type reagents, both accepted color-solubility tests for paint classifications.

The utility of the Le Rosen reagent was investigated with a number of white paints because rapid differentiation between unknowns of this common paint color (of almost ubiquitous distribution) is difficult. The differentiation of vehicle composition in various automotive and common household paint types by this method can be dramatic.

Materials and Methods

Reagents used in this study were prepared from certified American Chemical Society (ACS) acids, certified ACS formaldehyde solution, or Fisher certified diphenylamine. Concentrated sulfuric acid was used as supplied.

The diphenylamine reagent was prepared by adding a solution of 0.3 g of diphenylamine in 20 ml of sulfuric acid to 10 ml of glacial acetic acid.[2]

The Le Rosen reagent was prepared by adding ten drops of 37% formaldehyde to 10 ml of concentrated sulfuric acid.

The procedure of adding two drops of concentrated sulfuric acid to the test sample, followed by one drop of 37% formaldehyde solution (within 5 s) and stirring with a thin glass rod, was used as a comparative test.

All reactions were carried out in a white spot plate at room temperature with two or three drops of reagent; when necessary, samples were submerged with a glass rod. Colors listed in Table 1 are the subjective results of two independent analysts. Obviously, comparisons of two or more paint samples must be carried out side by side in a concurrent fashion.

Paint types and manufacturers are listed in Table 1; all automotive paint samples tested were products obtained from the National Bureau of Standards Reference Collection of Automotive Paints, Chemical Supplement. All other paints were applied as thin films to glass microscope slides and allowed to air dry.

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[2]FBI Laboratory, Washington, D.C., personal communication, 1977.

Results and Discussion

The Le Rosen test has wide application in organic analysis. Feigl [*1*] recommends it as a general test for aromatic compounds but notes its reaction with higher molecular weight alcohols (as are common in alkyd vehicles [*2*]) yielding yellows, browns, or red browns. Indeed, the possible reactions of sulfuric acid and formaldehyde may include oxidation, dehydration, carbonium ion formation, and halochromism [*1*, p. 156], and even with simple aromatics the composition of the colored products is not certain. A combination of simultaneous reactions and side reactions may yield widely varying colors with a material as complex as paint. This same test is widely used in the preliminary analysis of drugs, where it is known as the Marquis test [*3*].

Of the 30 paints used in this study 15 were household-type paints and 15 were automotive paints. The reactivities of these samples are given in Table 1. Most of these paints can be classified into one of six groups: household alkyd enamels, household acrylic enamels, household lacquers, automotive nonaqueous dispersion enamels, automotive acrylic solution lacquers, and automotive acrylic enamels. Paint samples were selected from each of the major American automotive manufacturers. Included within this collection are two groups of identical color, differing by vehicle composition, paint supplier, or both. The first is a group of five "Spinnaker" or "Eggshell" white paints used by Chrysler Corporation during 1976 and 1977 (Samples 16–20, Table 1). The second is a group of six paints used by GM during the 1976 and 1977 model years under various color designations (Samples 22–27, Table 1). Thus groups of widely varying vehicle composition, as well as groups of the same automotive color, were compared.

The following generalities can be drawn from the collected data. The Le Rosen test produces distinctive colors of darker and more vibrant shades than does sulfuric acid, and it produces colors in some cases where sulfuric acid does not. While sulfuric acid produced five groups of indistinguishable sets (1,4; 9,11; 13,14,15; 18,19,25,28,29; and 22,26), the Le Rosen test yielded four groups of indistinguishable paints each having only two members (1,4; 14,15; 18,19; 22,26). The addition of formaldehyde to sulfuric acid is not as effective as the use of the Le Rosen reagent directly. Lacquers[3] generally dissolved in the Le Rosen reagent while those paints with oxidizing, polymerizing, or coagulating vehicles did not. The diphenylamine test, while dramatic when applicable, does not often yield useful distinctions. It is also apparent from a comparison of Samples 7 and 8 (the acetone-soluble fractions of which are identical by infrared spectroscopy) that manufacturers do not necessarily list the correct composition of their products on the can; although marked otherwise, both of the Sapolin products are nitrocellulose lacquers. Similarly, products with trade name labels may in fact be indistinguishable from a large retailer's own brand (such as Specimens 1 and 4, which appear identical in composition and may be the same product sold under different labels).

By the Le Rosen test alone (but not with sulfuric acid alone) a rapid distinction can be obtained for one of the three paint samples distributed by the Forensic Sciences Foundation, Inc. as Specimens 10A, B, and C in the Laboratory Proficiency Testing Program (Samples 13–15, Table 1).

It is interesting to note that the Advisory Committee Supplementary Report [*4*] on these test samples indicates the Marquis (Le Rosen) test has "no basis for the characterization of paint and should be discontinued." In this supplement no criticism is made of the Le Rosen test; however, the Le Rosen test was reported in the initial summary of laboratory data [*5*] as discriminating Sample A from Samples B and C. (In that report at least three laboratories distinguished these samples by this method.)

[3]For the purpose of this study lacquers are defined as those coatings whose vehicle dissolves in acetone or chloroform.

TABLE 1—*A comparison of four color tests on various paint vehicles (white pigments).*[a]

Sample	Form	Manufacturer or Brand	Color	Color #	Composition of Vehicle	Color with Sulfuric Acid	Color with Diphenylamine	Color with Le Rosen Test	Color with (1) Sulfuric Acid and (2) Formaldehyde
1	spray enamel	New York Bronze Powder; Top Coat	gloss white	T9922	vinyltoluene soya alkyd resin, 5.66%; petroleum resin, 0.33%; additives, 0.11%	T → O	−T	Br → B	−Br
2	spray enamel	Zayre Supreme	flat white	none	vinyltoluene soya alkyd resin, 3.15%; additives, 0.23%	T	DT	DR → B	−DR
3	spray enamel	New York Bronze Powder; Plus	satin flat white	M-23	soya menhaden alkyd resin, 5.04%; acrylic copolymer resin, 0.24%; epoxy ester resin, 0.23%; additives, 0.34%	YT → T → dis	T → swells	YT → dis	YT → dis
4	spray enamel	Zayre	gloss white	1703	same as Sample 1	T → O	−T	Br → B	−Br
5	spray enamel	Du Pont; Lucite	gloss white	2400c	plasticized coconut-alkyd resin; cellulose esters; ester gum; total, 10%	Y → dis T	blue → dis	Y → dis T	YB
6	spray enamel	Sears Best	wrought iron white	65708	acrylic-castor-tall oil alkyd resin; total, 11.5%	Y	T	O → RO	−B
7	spray enamel	Sapolin	gloss white	135	soya alkyd and phenolic ether resins, 17.2%	Y → TO, dis	blue → dis	TO,dis→O	−O
8	spray lacquer	Sapolin	appliance white	121	coconut oil alkyd; cellulose nitrate; total, 8.9%	Y → O	blue → dis	O → T, dis	OT, dis
9	latex enamel	Benjamin Moore	satin white	33301	acrylic resin, 22.8%	NR, swells	NR	−P, swells	NR
10	enamel	Red Devil gloss white	white	none	soya alkyd resin, 17.9%	Y → Be, fades	T	Y, fades	T
10A	...	same as Sample 10	...	...	vehicle only	O → B	Y	Y → O → B	Y → B
11	latex enamel	Sears Best Interior semi-gloss	white	78885; 7834 tint	acrylic resin, 22%	NR, swells	NR	NR → −P, swells	NR

12	acrylic latex	Sears Best Weatherbeater	white	33015; 3301w	polyester resin, 3.1%; acrylic resin, 16.5%	C	slowly C	R	R
13	acrylic alkyd	FSF Proficiency Test 10A	white	none	acrylic alkyd	DC, dis	DC	Br	Br
14	soya alkyd	FSF Proficiency Test 10B	white	none	soya alkyd	DC, dis	B	Y	DC
15	soya alkyd	FSF Proficiency Test 10C	white	none	soya alkyd	DC, dis	B	Y	DC
16	nonaqueous dispersion enamel	Jones-Dabney	white	CN76A0033	...	OT	NR → slowly P	RO → DB	OT → RO
17	acrylic enamel	Jones-Dabney	white	CC76A0033	...	S	NR → slowly P	RO → OB	RO
18	acrylic enamel	Cook	white	KC76A0033	...	−PO	NR	O → T	−PO
19	nonaqueous dispersion enamel	Cook	white	KN76A0033	...	−PO	NR	O → T	−PO
20	acrylic enamel	Canadian Industries Ltd.	white	LC77A0033	...	O	NR	DO → B	−T
21	acrylic solution lacquer	Du Pont	white	DA76A0042	...	−Y → dis	NR	T, swells	−P
22	acrylic solution lacquer	Inmont	white	NA76A0044	...	dis → −P	NR → dis	dis→−P,D	NR
23	acrylic solution lacquer	Pittsburgh Plate Glass	white	PA76A0044	...	NR → dis	NR	dis −P	NR
24	water-based enamel	Inmont	white	NW76A0044	...	P → −O	NR	+O → B	−O
25	acrylic enamel	Du Pont	white	DC76A0044	...	PO	−P	−O	P

TABLE 1—*Continued.*

Sample	Form	Manufacturer or Brand	Color	Color #	Composition of Vehicle	Color with Sulfuric Acid	Color with Diphenylamine	Color with Le Rosen Test	Color with (1) Sulfuric Acid and (2) Formaldehyde
26	acrylic solution lacquer	Du Pont	white	DA76A0044	...	dis −P	NR	dis, P, D	dis −P
27	acrylic dispersion lacquer	Du Pont	white	DB76A0044	...	−Y → disP	NR, dis	Be, dis	−D
28	nonaqueous dispersion enamel	Cook	white	KN76A0123	...	PO	NR	+O → RB	−P
29	nonaqueous dispersion enamel	Cook	white	KN76A0163	...	PO	NR	PO → O	−P
30	nonaqueous dispersion enamel	Canadian Industries Ltd.	white	LN77A0163	...	P	NR	DO	−D

[a] Abbreviations:

B = brown
Be = beige
Br = brick red
C = cream
D = dark or darkening
dis = dissolves
FSF = Forensic Sciences Foundation
NR = no reaction
O = orange
P = pink
R = red
S = salmon
T = tan
Y = yellow
+ = bright
− = light
→ = goes to

Summary

In comparative analysis the Le Rosen test offers rapid discrimination between many white pigmented paint vehicles and should be considered as a useful addition to other common spot tests for paint.

References

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[3] Clarke, E. G. C., *Isolation and Identification of Drugs,* Pharmaceutical Press, London, 1969, pp. 133, 663-669.
[4] "Laboratory Proficiency Testing Program, Supplementary Report, Samples 6-10," The Forensic Sciences Foundation, Inc., Rockville, Md., July 1976, p. 12.
[5] "Laboratory Proficiency Testing Program, Report No. 10, Paint Examination," The Forensic Sciences Foundation, Inc., Rockville, Md., 1976.

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