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Pyrolysis-Gas Chromatographic Analysis of Automobile Paints

The problem facing the forensic scientist in the examination of paint as physical evidence is the limited amount of information that can be obtained from trace samples. Examination of the paint involves tests to determine the composition of the binder. These tests include spot tests which differentiate between binders by solubility and color reactions [*1*] and infrared spectroscopy which identifies the functional groups present in the sample [*2*]. Pyrolysis-gas chromatography can also be used to compare paint traces with the suspected source or, by reference to standard chromatograms, to identify the type of binder. In addition, the identity of the manufacturer of the paint smear and, in many cases, the make of automobile as well as the year, can be determined by the pyrolysis of small paint samples.

The method described in this report involves the pyrolysis-gas chromatographic analysis of the 1973 automotive finishes, and the classification of the finishes by manufacturer.

The majority of the binders, and almost all automotive finishes, are composed of polymers which are built up either during manufacture or during the drying process [*3*]. Pyrolysis-gas chromatographic techniques have been used extensively for the identification of copolymers and mixed polymers. Groten [*4*] examined over 150 different polymers, including synthetic resins, mixed polymers, and copolymers, and although similarities were found among some, he was able to distinguish all the samples. Strassburger et al [*5*] showed that copolymers of methyl methacrylate could be distinguished from polymer mixtures of the same composition by the differences in intensity and that constituents of copolymers in concentrations as small as 0.2 percent could be detected. O'Mara [*6*] demonstrated the qualitative and quantitative reproducibility of pyrolysis gas chromatography in the study of poly (vinyl chloride) using a combined gas chromatography-mass spectrometry system. Jain et al [*7*] examined 34 commercially available coatings, including house paints, automotive finishes, and primers, and were able to distinguish all but two of the coatings.

Experimental

Equipment

The analyses were made with a Fisher-Victoreen gas chromatograph equipped with a reactor tube pyrolyzer and a Model 4010 digital log electrometer. The full scale range of the

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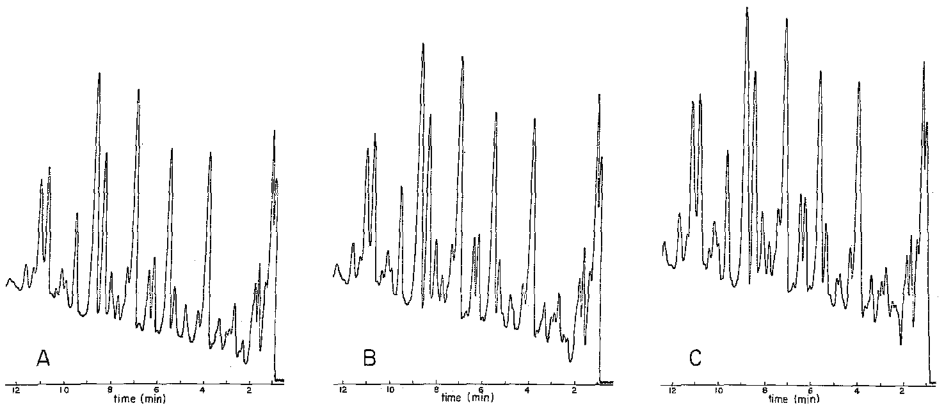

FIG. 1—*The effect of sample size: (A) 0.05 mg, (B) 0.10 mg, (C) 0.25 mg.*

recorder represents four decades of ion current from the hydrogen flame ionization detector, covering the range of 10^{-11}A to 10^{-7}A. The advantages of the logarithmic display for the analysis of complex mixtures have been demonstrated by Byrnes [*8*] and Chisum and Elzerman [*9*].

A combination column comprised of an 8 ft by ⅛ in. 15 percent Carbowax 20M, on 80/100 AW-DMCS treated Chromosorb W, followed by a 3 ft by ⅛ in. 10 percent silicone Dow Corning 200, on 80/100 AW-DMCS treated Chromosorb W, performed the separation of the thermal degradation products. The programming begins at the start of the pyrolysis and the column is held at 50°C for 2 min, at which time the column temperature is increased 15°C/min until 180°C and held there for 5 min.

Procedure

Paint panels received from the manufacturers were used for the analysis. These panels were representative of the production batches, and thus were the same quality as the automobile finish. The finish layer was scraped off the panel with a scalpel and weighed. A sample size of 0.1 mg was chosen for the analysis but, as shown in Fig. 1, a wide range of sample sizes gave essentially identical information. The reactor tube pyrolyzer design, which provided uniform heating at a rate of 200°C/s coupled with the logarithmic output, minimized possible variations due to sample size.

A pyrolysis temperature of 400°C was chosen to effect the thermal degradation of the paint sample. The chromatograms obtained upon pyrolyzing two different types of acrylic enamels at 300°C, 400°C, 600°C, and 800°C are shown in Fig. 2 and, as previously demonstrated by Lehmann and Brauer [*10*], show the increase in the number of products with temperature. This increase in degradation products does not imply an increase in the differences of the two enamels as shown by the nearly identical results at 800°C.

Columns with stationary phases of different polarity were also tried in an attempt to distinguish the paints. These included SE-30 (non-polar), Dinonyl phthalate (intermediate), and Carbowax 20M (polar) stationary phases, and the ability to distinguish the paints increased with increasing polarity. The column selected gave results similar to the Carbowax 20M column, but the rapidly eluted gaseous products were separated on the combination column.

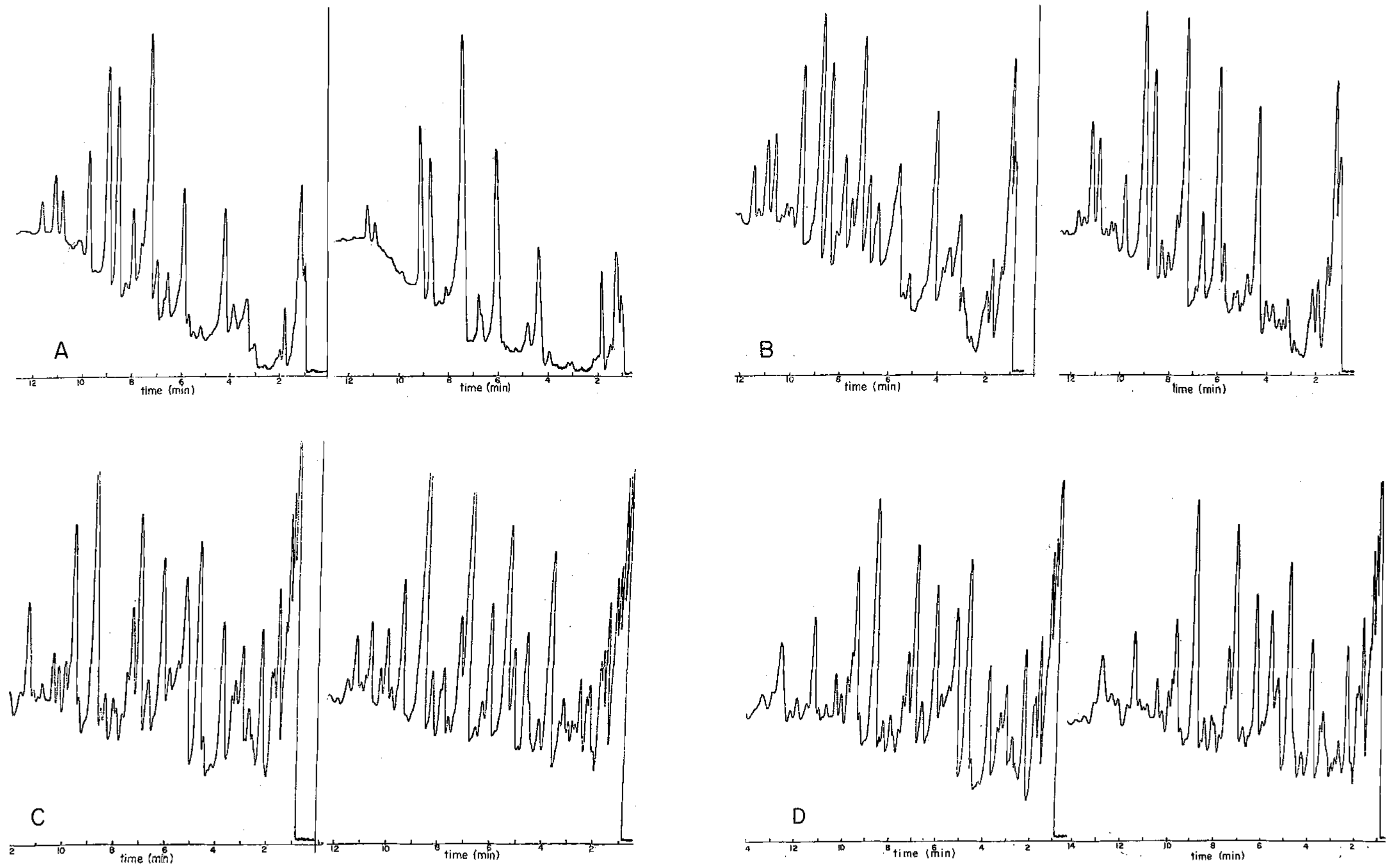

FIG. 2—*Comparison of Chrysler Corp. Type 2 NAD (right) and American Motors Type 1 NAD (left) as a function of pyrolysis temperature: (A) 300°C, (B) 400°C, (C) 600°C, (D) 800°C.*

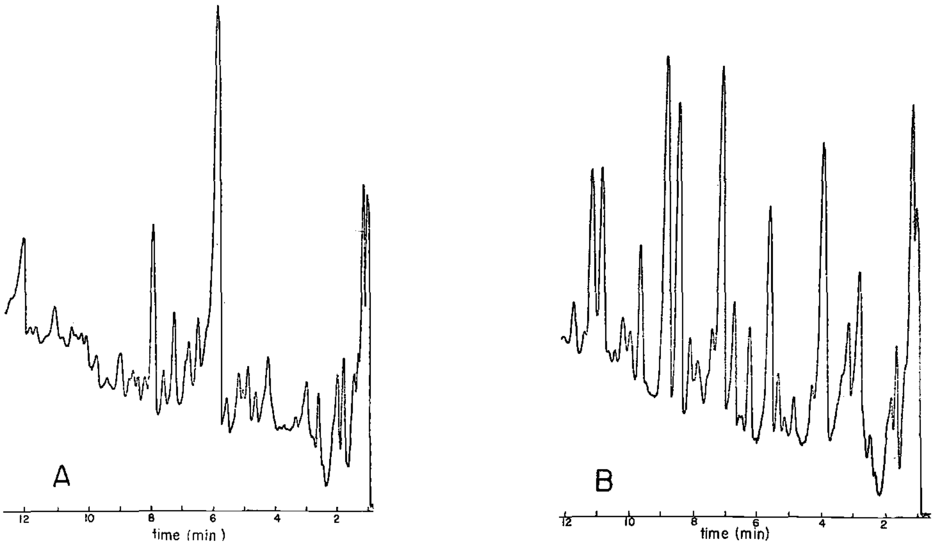

FIG. 3—*Difference between acrylic lacquer and acrylic enamel finishes: (A) General Motors Corp. lacquer, (B) Ford Motor Co. enamel.*

Results and Discussion

The binders in the automotive finishes currently used by American manufacturers are composed of either thermoplastic acrylic resins or thermosetting acrylic resins. General Motors automobiles have thermoplastic acrylic lacquer finishes and the remaining three manufacturers (Ford, Chrysler, and American Motors) have thermosetting acrylic enamel finishes. The chromatograms of a typical acrylic lacquer and enamel, shown in Fig. 3, are quite different.

Acrylic Enamel Finishes

For the 1973 model year, Chrysler Corp. and American Motors Corp. use the new dispersion finishes exclusively. These nonaqueous dispersion finishes (NAD) are different from the solution-type finishes in the nature of the vehicle, that is, the solvents and binders. The polymer, which is maintained in suspension in a liquid composed of solvents and non-solvents, is in the form of very small (<1 μm) particles. This solid suspension results in at least a 30 percent higher concentration of solids at the spray gun and enables two-coat application, rather than the current application of three coats, to achieve desired film thickness.

Cook Paint and Varnish Co. and Pittsburgh Plate Glass (PPG) Industries have both developed NAD finishes. The Cook formulation, or Type 1 NAD, is the basis for all American Motors automobiles. Regardless of supplier, the Type 1 formulation must be followed. Figure 4 shows examples of the Type 1 NAD finishes supplied to American Motors by the various manufacturers and, although slightly different, all three chromatograms have similar characteristics. The PPG formulation, or Type 2 NAD, is the basis for all Chrysler Corp. metallic finishes and the Type 1 formulation is used for all nonmetallics. Figures 5 and 6 demonstrate the adherence to this requirement by the manufacturers. As

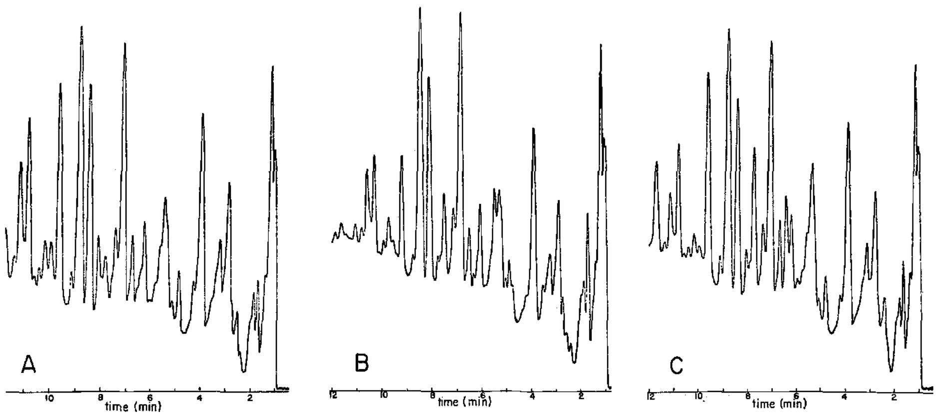

FIG. 4—*Type 1 NAD finishes supplied to American Motors Corp.: (A) Cook Paint and Varnish Co., (B) PPG Industries, (C) Celanese Coatings Co.*

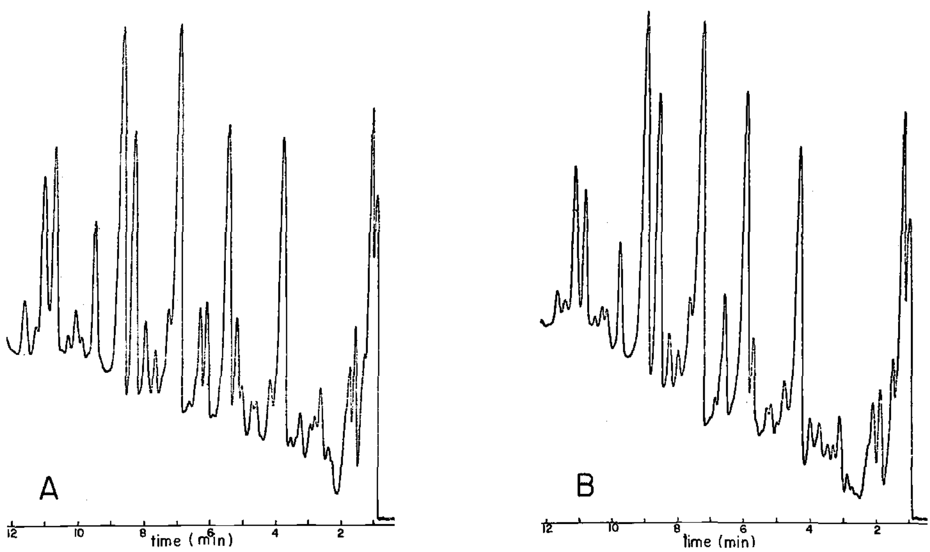

FIG. 5—*Type 2 NAD metallic finishes supplied to Chrysler Corp.: (A) PPG Industries, (B) Celanese Coatings Co.*

would be expected, the Chrysler Corporation nonmetallics are quite similar to the American Motors finishes.

The Paint and Vinyl Operations of Ford Motor Co., which supplies the majority of paint to Ford, has also developed an NAD-type finish. Three metallic blue dispersion finishes, one from each automotive manufacturer, are shown in Fig. 7. All three NAD finishes can be distinguished both by peak intensity and peak location. Ford Motor Co. also uses the solution-type enamel at a large number of the assembly plants. Three practically identical metallic brown finishes, one from each automotive manufacturer (but with the

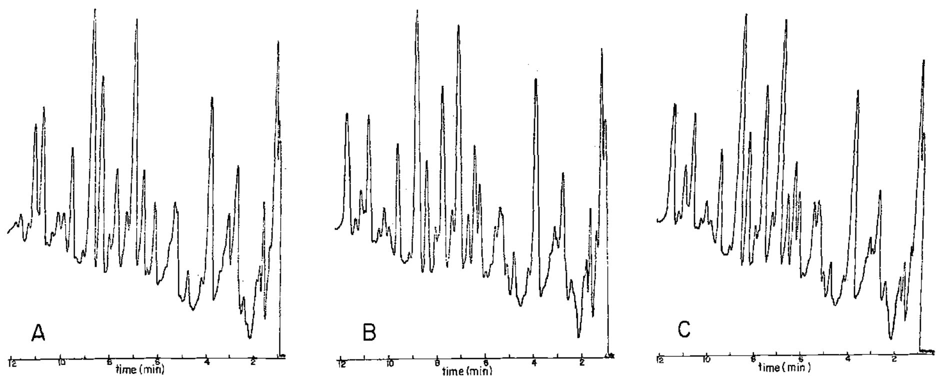

FIG. 6—*Type 1 NAD nonmetallic finishes supplied to Chrysler Corp.: (A) PPG Industries, (B) Celanese Coatings Co., (C) Cook Paint and Varnish Co.*

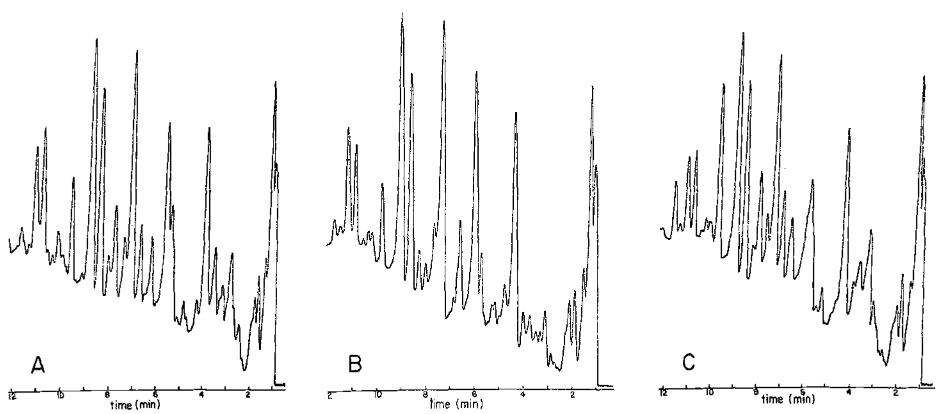

FIG. 7—*Comparison of similar blue metallic dispersion-type finishes: (A) Ford Motor Co., (B) Chrysler Corp., (C) American Motors Corp.*

Ford panel being a solution-type enamel supplied by Paint Operations), are shown in Fig. 8. All three are easily distinguished.

Ford Motor Co. paints automobiles in at least 17 different plants in the United States and Canada, and utilizes a number of suppliers for the same color. The six chromatograms of Fig. 9 represent different acrylic enamels used at the various plants for the white enamel finish. If a sufficient sample is present to identify color, the number of possible locations from which the automobile originated can be reduced and, coupled with the production schedule, the type of Ford Motor Co. automobile can be identified. Chrysler Corp. and American Motors Corp., which have fewer assembly plants, use a single supplier for a given color for all but a very few colors.

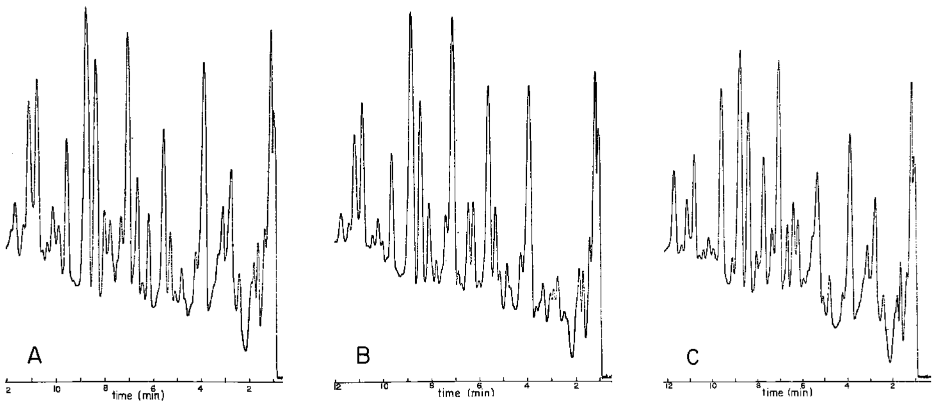

FIG. 8—*Comparison of similar brown metallic finishes: (A) Ford Motor Co. solution-type finish, (B) Chrysler Corp. dispersion-type finish, (C) American Motors dispersion-type finish.*

Acrylic Lacquer Finishes

E. I. du Pont de Nemours and Co., Inmont Corp., and PPG Industries supply automotive finishes to General Motors and identification of the three suppliers is possible, as shown in Fig. 10. The majority of the General Motors Assembly Division plants and the Fisher Body plants uses one source exclusively for all colors and thus, like Ford Motor Co., the number of possible locations from which the automobile originated can be reduced, and in some cases the make of the General Motors automobile can be determined. The common formulation for all the General Motors automotive division's finishes, added to the fact that du Pont is the major source for the majority of the plants, limits the amount of information that can be obtained.

Summary

A technique for the classification and comparison of automotive finishes using pyrolysis-gas chromatography has been presented. The 1973 model automotive finishes were studied and the ability to distinguish the finishes by automobile manufacturer was shown. The decision by Chrysler Corp. and American Motors Corp. to use different formulation NAD finishes for 1973 facilitates identification of their automobiles. Ford Motor Co. can also be distinguished since the majority of the finishes are Ford formulation solution or dispersion finishes. The remaining enamel finishes supplied to Ford Motor Co. can be identified by the manufacturer and distinguished from the Chrysler and American Motors automobiles. General Motors Corp. uses a completely different binder system and is easily distinguished from the other manufacturers.

Further research is being undertaken to distinguish the earlier model years and to determine if the paint batches can be distinguished. Cryogenic cooling, which should result in better separation and analysis of the lighter molecular fragments, will be used in the attempt to distinguish the paint batches.

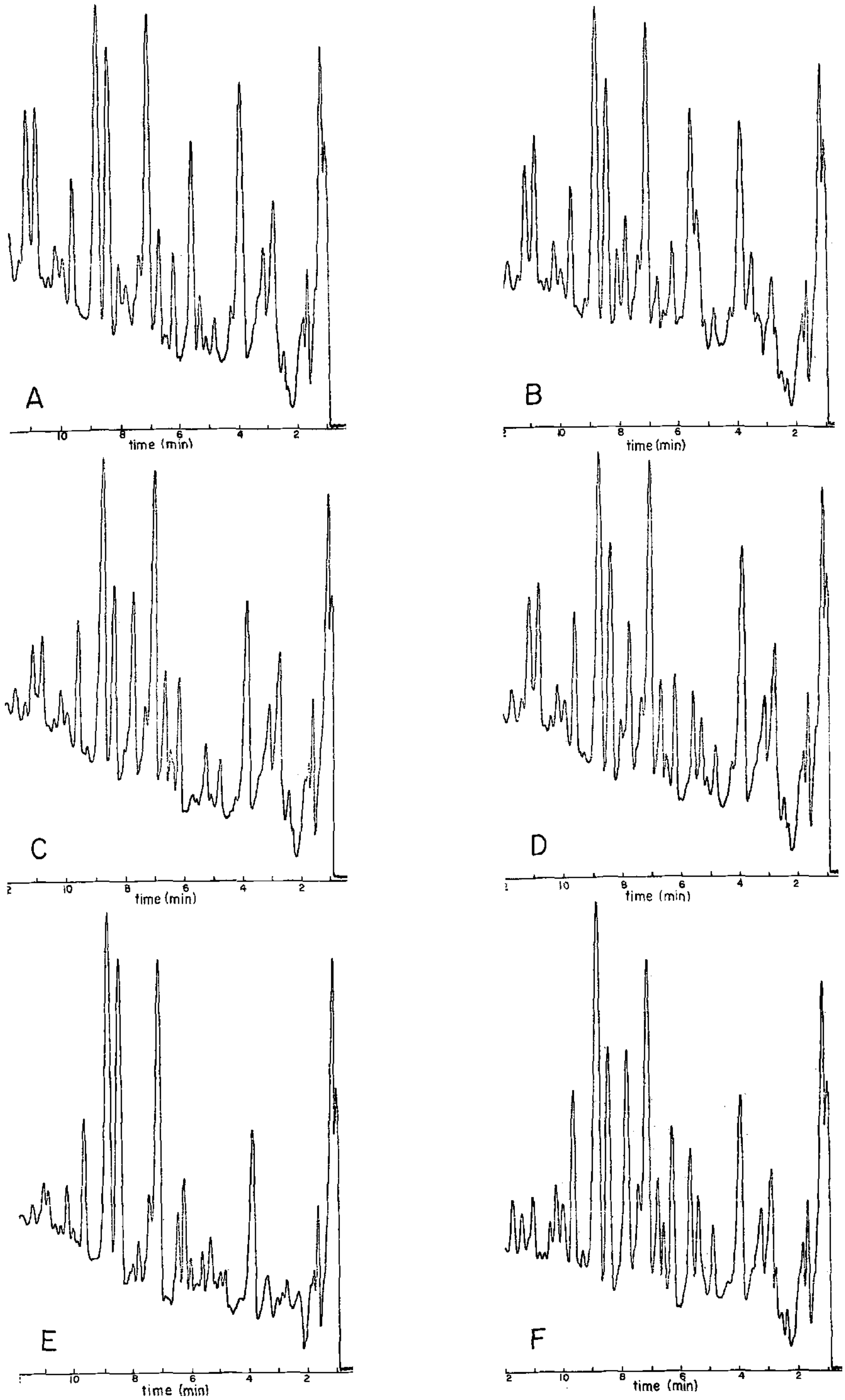

FIG. 9—*Ford Motor Co. white enamel finishes: (A) Ford solution-type, (B) Ford dispersion-type, (C) Cook heavy solids, (D) Cook solution-type, (E) Inmont solution-type, (F) Celanese solution-type.*

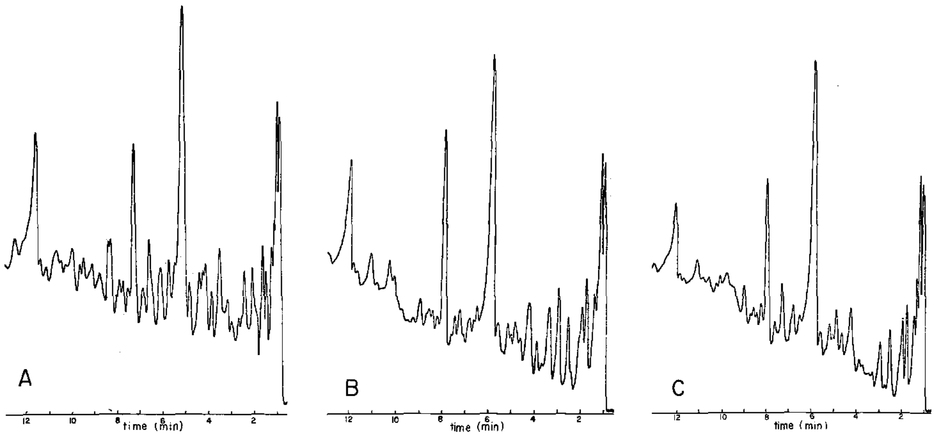

FIG. 10—*General Motors Corp. acrylic lacquer finishes: (A) Du Pont Co., (B) Inmont Corp., (C) PPG Industries.*

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