Analysis of Nail Lacquers

Most opaque nail lacquers are solutions of nitrocellulose, plasticizers, and resins in mixed volatile organic solvents. Color and opacity are produced by pigments suspended in the lacquer.

In nail lacquers, *n*-butyl phthalate, camphor, and tricresyl phosphate are common plasticizers; an aryl sulfonamide-formaldehyde polymer is a frequently used resin, and the pigments are likely to be organic lakes, guanine, and titanium dioxide. The solvents are usually mixtures of toluene, butyl acetate, ethyl acetate, ethanol, and isopropanol.

A typical nail lacquer contains about 12% nitrocellulose, 5% *n*-butyl phthalate, 5% aryl sulfonamide-formaldehyde resin, 1–3% camphor, and 1–2% pigment. The solvent may approximate 35% toluene, 40% butyl acetate, 15% ethyl acetate, and 10% ethanol.

General Analysis

1 Net Contents

Remove the brush and cap from the bottle and mark the height of the liquid on the outside of the bottle. When analysis has been completed, empty the bottle, rinse it with acetone, and fill it with water to the previously inscribed mark; then empty the water into a graduated cylinder and record the volume of liquid.

2 Description of Nail Lacquer

Note color, odor, opacity, and other physical characteristics of the nail lacquer.

3 Infrared Film Spectrum of the Nail Lacquer

(a) Prepare a sample by coating a salt crystal with a thin film of the lacquer and drying at 105°C in an oven for 5 minutes.

(b) Observe whether the infrared spectrum can be interpreted as a mixture of nitrocellulose, *n*-butyl phthalate, and aryl sulfonamide-formaldehyde resin.

4 Non-volatile Matter at 105°C

After discarding the brush from the bottle top, weigh the closed bottle of nail lacquer. Pour about 1.0–1.2 g in a tared weighing bottle 65 mm high and 45 mm in diameter, and weigh the nail lacquer bottle again. The difference in weight is the sample weight. With the top removed, manipulate the weighing bottle so that the lacquer covers the entire inside surface of the bottle as a thin film. Then heat the lacquer at 105°C in an oven for 2 hours. Cool and weigh the residue as non-volatile matter.

5 Determination of Non-volatile Constituents

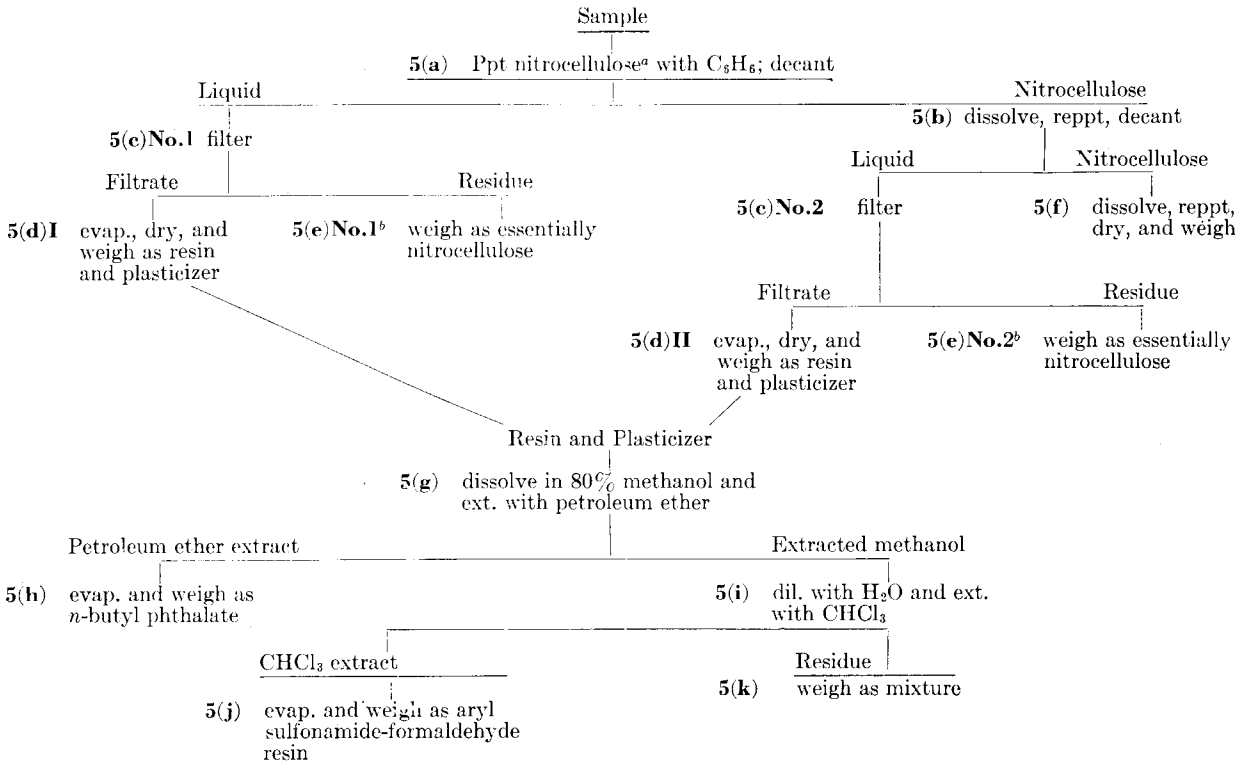
The overwhelming majority of commercial nail lacquers contain these non-volatile components: nitrocellulose, organic lakes, inorganic pigments such as TiO_2, *n*-butyl phthalate, and an aryl sulfonamide-formaldehyde resin. The following is a method of analysis (see Chart 1) for these nail lacquer ingredients:[1]

(a) Dilute a 4–6 g sample with 5 ml of acetone, add 20 ml of benzene, and pour slowly with stirring into a 400 ml beaker containing 150 ml of hot benzene. Rinse the sample container with 5 ml of acetone and add the rinsings to the benzene. Evaporate the benzene on the steam bath under a gentle jet of air to about 80 ml, dilute with 90 ml of benzene, and cool to room temperature. Pour the mixture into a centrifuge tube, rinse the precipitation beaker with 10 ml of benzene, and add the rinsings to the centrifuge tube. Reserve the precipitation beaker and any precipitate that adhered to the sides. After centrifuging, decant the supernatant liquid into a 250 ml beaker labeled No. 1 and set it aside.

(b) Dissolve the residue in the precipitation beaker and the centrifuge tube from (a) with 15, 10, and 10 ml portions of acetone, and pour the combined acetone solutions into a 100 ml beaker. Evaporate the acetone on the steam bath, redissolve the residue in 10 ml of acetone, add 20 ml of benzene, and repeat the precipitation and centrifuging procedure described in (a). Decant the supernatant liquid into a beaker labeled No. 2. Reserve the precipitation beaker and the centrifuge tube containing the residues.

[1] *J. Assoc. Offic. Agr. Chemists.* **38**, 524 (1955). A number of chemical tests for nail lacquer components are described in *Ind. Eng. Chem., Anal. Ed.*, **16**, 541 (1944).

Chart 1. Diagrammatic scheme of colored nail lacquer analysis



[a] Colors (1-2%) will be precipitated and carried along with the nitrocellulose.
[b] In practice, fractions (e)No. 1 and (e)No. 2 are combined and weighed as one fraction.

(c) Filter the decanted liquids in beakers No. 1, (a), and No. 2, (b), through the same 12.5 cm S&S No. 597 filter paper into two tared beakers labeled I and II. Reserve the filter paper and beakers Nos. 1 and 2.

(d) Evaporate the filtrates in beakers I and II, (c), on the steam bath under jets of air, and dry the residues in an oven at 105°C for 10 minutes. Cool, and weigh I and II as combined resin and plasticizer.

(e) Rinse the reserved beakers Nos. 1 and 2, (c), with two 30 ml portions of hot methyl ethyl ketone and pour the rinsings through the reserved filter paper, (c), into a tared beaker. Discard the filter paper, evaporate the filtrate on the steam bath under a jet of air, dry the residue in an oven at 105°C for 20 minutes, cool, and weigh as a mixture consisting essentially of nitrocellulose and pigments.

Obtain an infrared film spectrum of the residue from a film prepared in the following manner: Dissolve a little of the material in acetone, pour some of the solution on a salt crystal, let the acetone evaporate in air, dry the film on the crystal in an oven at 105°C for 5 minutes, and cool to room temperature.

(f) Dissolve the residues in the reserved precipitation beaker and the centrifuge tube, (b), in acetone, and transfer the acetone solutions to a tared 250 ml beaker. Evaporate the acetone on the steam bath, redissolve the residue in 5 ml of acetone, and add 75 ml of alcohol-ether solution (1+2) followed by 10 ml of water. Evaporate the solvent on the steam bath under a gentle jet of air and dry the residue in an oven at 105°C for $1^1/_2$hours. Cool, and weigh as nitrocellulose plus pigments.

Obtain an infrared film spectrum of the residue as described in (e).

(g) Use 32 ml of methanol to dissolve and transfer the resin and plasticizer residues in beakers I and II, (d), into a 250ml separatory funnel. Add 8 ml of water and extract with four 40 ml portions of petroleum ether. Reserve the extracted methanol solution. Set the separatory funnels aside for rinsing later.

(h) Filter the combined petroleum ether extracts, (g), through a 12.5 cm S&S No. 597 filter paper into a tared 250 ml beaker. Follow with an additional 40 ml of petroleum ether wash through the filter paper. Reserve the filter paper. Evaperate the filtrate on the steam bath under a jet of air, dry the residue in an oven at 105°C for 10 minutes, cool, and weigh as butyl phthalate.

Obtain an infrared film spectrum of the material from a liquid film spread on a salt crystal. Also obtain the ultraviolet spectrum of an alcohol solution of the phthalate.

(i) Transfer the reserved extracted methanol solution, (g), to a 500 ml separatory funnel, add 50 ml of chloroform, dilute with 200 ml of water, and acidify with a little HCl. Shake the mixture well and draw off the chloroform layer. Continue the extraction with additional 50, 50, and 30 ml portions of chloroform. Reserve the extracted aqueous solution. Set the separatory funnel aside for rinsing later.

(j) Filter the combined chloroform extracts, (i), through the reserved filter paper, (h), and follow with an additional 40 ml wash with chloroform. Reserve the filter paper. Evaporate the filtrate on the steam bath under a jet of air, dry the residue in an oven at 105°C for 10 minutes, cool, and weigh as aryl sulfonamide-formaldehyde resin.

Obtain an infrared film spectrum of the resin as described in (e). Also obtain an ultraviolet spectrum of an alcohol solution of the material.

(k) Filter the extracted aqueous solution, (i), through the reserved filter paper, (j). Discard the filtrate. Rinse all the separatory funnels used in the extractions, (g) and (i), with two 30 ml portions of acetone, and filter the acetone solutions through the filter paper into a tared 250 ml beaker. Discard the filter paper. Evaporate the filtrate on the steam bath, dry the residue in an oven at 105°C for 10 minutes, cool, and weigh as a mixture of resin and nitrocellulose.

Obtain an infrared film spectrum of the material as in (e).

6 *Separation of Nitrocellulose from Pigments*

(a) *Guanine.*—The mother-of-pearl appearance of some nail lacquers arises from the presence of guanine. To analyze such a product, dilute a weighed sample with acetone, centrifuge, and decant the acetone. Use the acetone solution for the procedure described in 7.5. Indentify the guanine residue from the infrared spectrum of a mineral oil mull or from a film prepared by rubbing the guanine between two salt crystals with a drop of acetone. Separate the crystals and evaporate the acetone at 105°C in an oven.

(b) *Opaque colored nail lacquers.*—The opaque colored effect[2] is achieved through the

[2] The analysis of several commercial samples indicates that the amount of coloring material present in nail lacquers varies from 1 to 2%.

dispersion of finely divided organic lakes[3] and inorganic pigments such as TiO_2. The nitrocellulose may be separated from the coloring agents by the following procedure:[4]

Dissolve, disperse, and transfer the residues of precipitated nitrocellulose and pigments, from **5(e)** and **5(f)**, into a 50 ml heavy-duty centrifuge tube with the aid of 25 ml of hot methyl ethyl ketone. Add 4 drops of water and 50 mg of silicic acid (Mallinckrodt's chromatographic grade) to the solution. Centrifuge at high speed for one hour (an International Clinical Centrifuge, Model No. 434, is satisfactory) and decant the supernatant liquid into a 250 ml separator. Treat the residue in the centrifuge tube with successive 15 and 10 ml portions of methyl ethyl ketone, centrifuging 15 minutes each time and decanting as before into the separator. Discard the residue in the centrifuge tube.

Add 1 ml of HCl to the separator, shake 2–3 minutes, and extract with 50 ml of water saturated with methyl ethyl ketone. Discard the extract. Make the methyl ethyl ketone solution slightly basic with ammonia and extract with 50 ml of an aqueous solution which is weakly ammoniacal and saturated with the ketone, and which contains 0.5% ammonium chloride. Continue the alkaline extracts until no further color is extracted (three extractions usually suffice). Discard the extracts, re-acidify the ketone solution with HCl, and wash with two 25 ml portions of water which is weakly acid with HCl and saturated with the ketone. Discard the washings.

Filter the extracted methyl ethyl ketone solution through an 11 cm S&S No. 597 filter paper into a 250 ml tared beaker. Wash the separator and the filter paper with two 25 ml portions of hot methyl ethyl ketone, collecting the washings in the tared beaker.

Evaporate the volatile solvent on the steam bath under a gentle jet of air. Redissolve the residue in 5 ml of acetone and add 75 ml of alcohol-ether solution (1+2) followed by 10 ml of water. Again evaporate the solvent on the steam bath under a gentle jet of air and dry at 105°C in an oven for 1½ hours. Cool, and weigh as nitrocellulose.

(In separating the nitrocellulose and the pigments from the nail lacquers, traces of pigment may adhere to the sides of the glassware or on the filter paper. These traces can be dissolved by alcohol strongly acidified with HCl.)

7 Tricresyl Phosphate in Nail Lacquers

When tricresyl phosphate is used with *n*-butyl phthalate as the plasticizer, the two substances are isolated together (see **7.5(h)**). The infrared spectra of these two materials differ sufficiently so that each can be identified in the presence of the other. If it is necessary to determine the amount of each component, the ultraviolet spectra differ enough so that the methods for the analysis of two-component mixtures can be applied.

8 Acrylonitrile-Butadiene Polymer

An acrylonitrile-butadiene polymer may be detected in the infrared spectrum of the non-volatile matter. The CN absorbance peak is at 4.45μ.

When the polymer is present as an additional ingredient in a nail lacquer, it is isolated by precipitation with methanol. The methanol solution may be used for the usual nail lacquer analysis.

9 Base Coats

(a) Base coats are preparations which are applied prior to the nail lacquer. They are usually solutions of polymeric substances. The polymers are most readily recognized by examination of the infrared spectrum of the non-volatile matter. Ultraviolet spectra, sometimes of films on a quartz surface, are also helpful if the polymers have aromatic constituents. When a base coat contains two or more polymers, it is good practice to separate them, e.g., by extraction.

(b) Acrylonitrile-butadiene and phenol-formaldehyde polymers are among those used in base coats.

Infrared Spectrophotometric Analysis

10 Description and Interpretation of Spectra

Description and interpretation of some infrared spectra are helpful in the analysis of nail lacquers. A commercial colorless nail lacquer, known to contain nitrocellulose, *n*-butyl phthalate, and aryl sulfonamide-formaldehyde resin as non-volatile ingredients, was analyzed.

The infrared spectra of the following fractions were examined.

[3] A procedure for the identification of the organic lakes used in nail lacquers is given in *Proc. Sci. Sec. Toilet Goods Assoc.*, **11**, 20 (1949).

[4] *J. Assoc. Offic. Agr. Chemists*, **39**, 259 (1956).

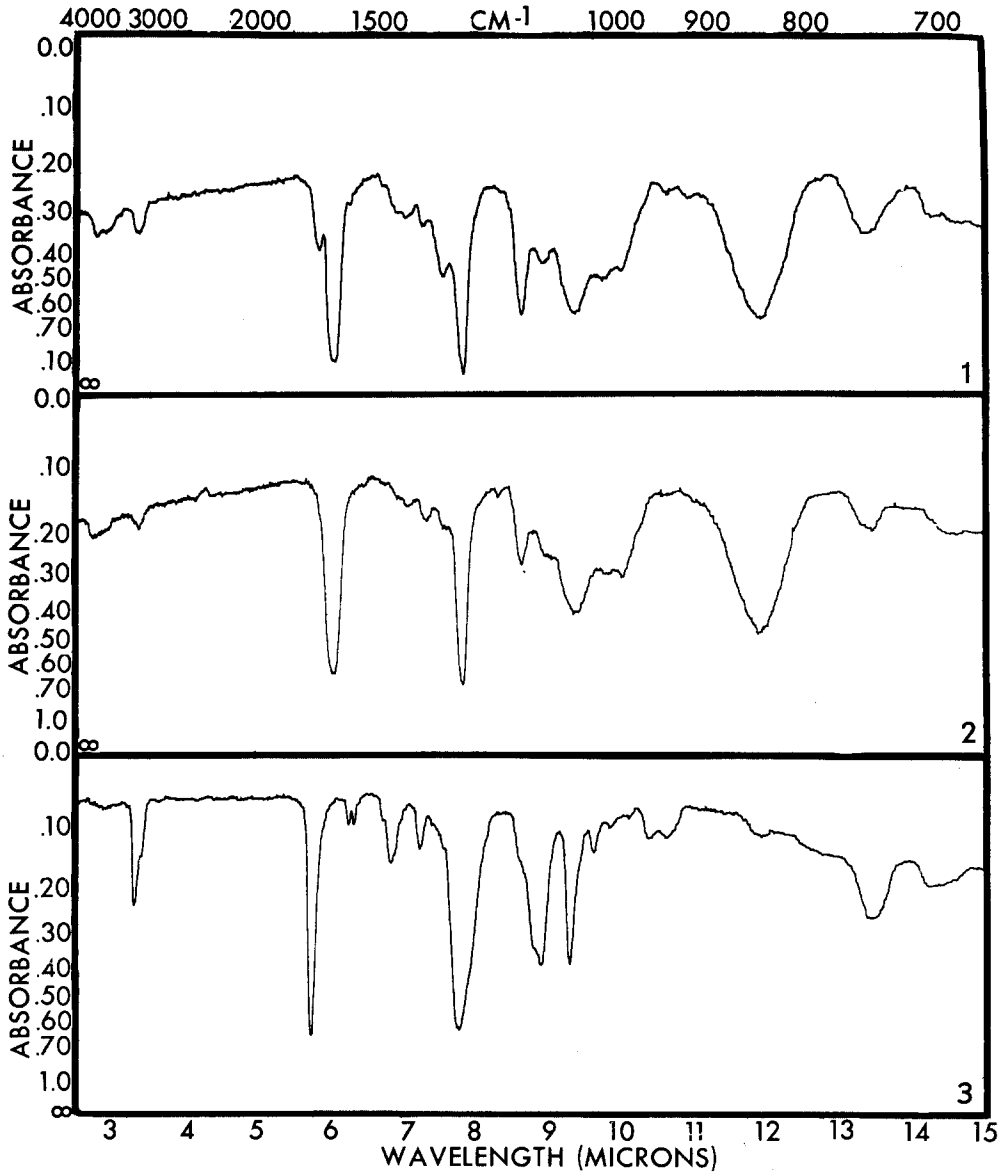


Fig. 1 —Infrared spectrum of a film of non-volatile matter at 105°C derived from commercial nail lacquer.
Fig. 2 —Infrared spectrum of a film of nitrocellulose derived from commercial nail lacquer.
Fig. 3 —Infrared spectrum of a film of *n*-butyl phthalate derived from commercial nail lacquer.

(a) *Non-volatile matter.*—Represented by Fig. 1

(1) The presence of nitrocellulose is immediately apparent from the absorption maximum just beyond 6μ and the one at 12μ.

(2) Although there is no positive identification for *n*-butyl phthalate, the indication of carbonyl absorption at 5.85μ suggests that it might very well be a constituent of the product. Likewise the absorption at 8.6μ may arise from an aryl sulfonamide-formaldehyde resin.

(b) *Nitrocellulose.*—Represented by Fig.

2 , This spectrum is very similar to the published spectra of nitrocellulose.

(1) The principal absorption maxima at 6.05 and 7.8μ are characteristic of the covalent nitrate groups. The strong absorption at 11.9μ is also associated with the nitrate group and that at 9.4μ with the cellulose ring. Note the broad but weak OH absorption just before 3μ and the weak C—H absorption just before 3.5μ. The minor absorption maxima also aid in identifying nitrocellulose.

(2) In the analysis of colored opaque nail lacquers containing suspended pig-

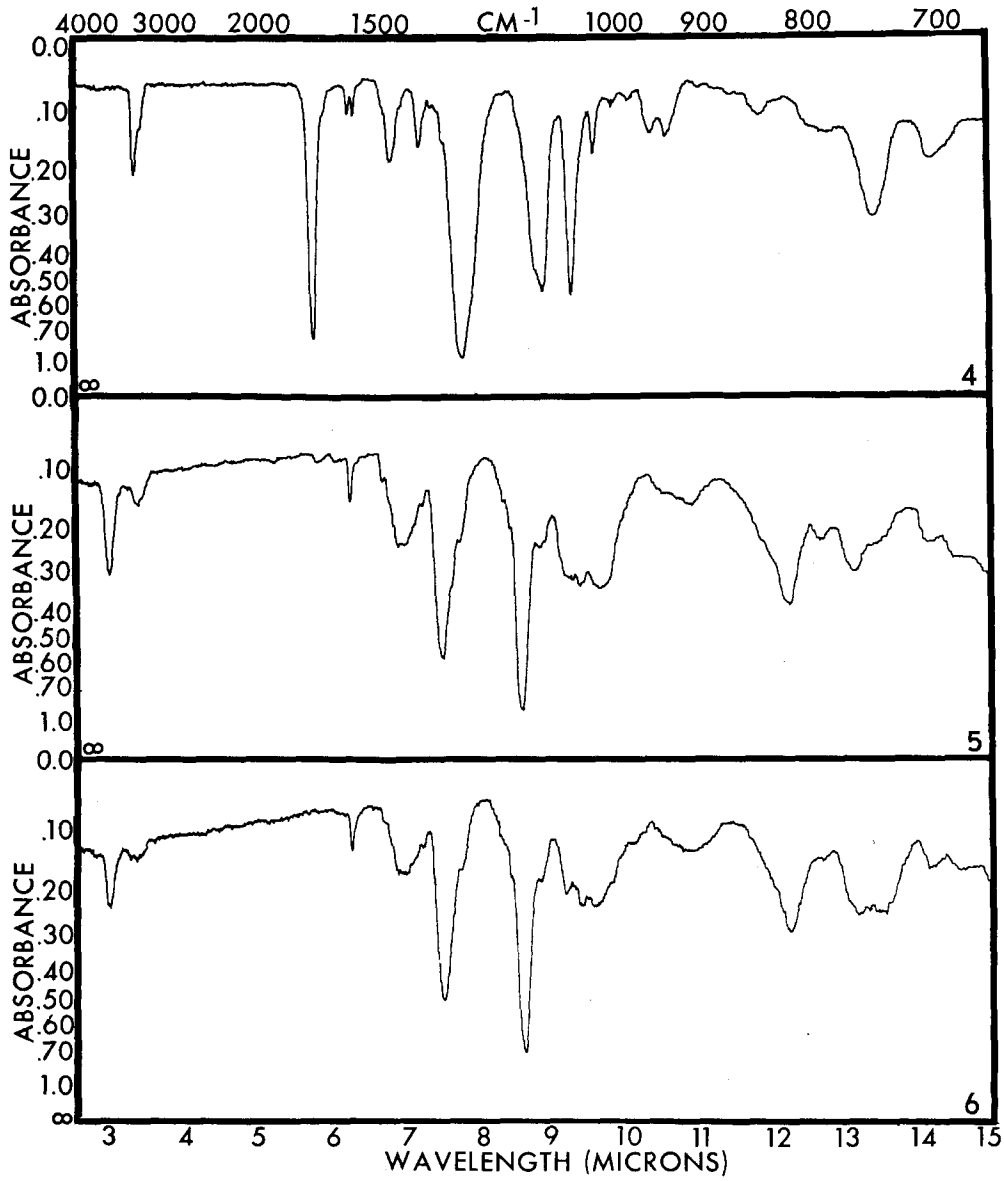


Fig. 4 —Infrared spectrum of a film of *n*-butyl phthalate.
Fig. 5 —Infrared spectrum of a film of aryl sulfonamide-formaldehyde resin derived from commercial nail lacquer.
Fig. 6 —Infrared spectrum of a film of Santolite-M-H-P (Monsanto).

ments, the precipitation of the nitrocellulose entrains the pigments. However, it is difficult to differentiate the infrared film spectrum of the contaminated nitrocellulose from that of pure nitrocellulose. In part this is due to the small amount of pigment, 1–2%, ordinarily present in nail lacquers.

(c) *n-Butyl phthalate.*—Represented by Fig. 3 . The spectrum of an authentic sample of *n*-butyl phthalate is given in Fig. 4 .

(1) The characteristic strong absorption maxima of phthalates are the carbonyl ester absorption at 5.8μ and the maxima at 7.8, 8.9, and 9.3μ. The weak doublet centered around 6.3μ always appears in phthalates. The other absorption peaks are also helpful for identification.

(2) The intensity of the C—H absorption in the 3.5μ region is indicative of the length of the alkyl carbon chain of the ester.

(d) *Aryl sulfonamide-formaldehyde resin.*—Represented by Fig. 5 . Figure 6 is the spectrum of a commercial sample of the resin sold under the trade name of "Santolite-M-H-P."[5]

(1) The major absorption maxima attributable to sulfonamides appear at 7.5 and 8.6μ. The weak C—H absorption in the 3.5μ region as well as the relatively strong absorption between 12 and 15μ indicates the aromatic nature of the material. The weak but sharp absorption peak just before 3μ suggests N—H linkages. The absorption at other wavelengths aids in uniquely identifying the resin.

(2) There is some difference in absorption between the commercial and isolated resins in the 13.5μ region. The resin may be slightly altered chemically, in the course of the analysis, or else some component of the resin may be lost in the extraction procedure.

11 *Infrared Spectra of Guanine and Tricresyl Phosphate*

(a) *Guanine from commercial nail lacquer.*—Represented by Fig. 7 . Spectra of a known sample of guanine obtained by heating the hydrochloride to 200°C are given by Figs. 8 and 9

Guanine has many identifying absorption maxima. Two readily recognizable linkages are the N—H absorption between 2.9 and 3.5μ and carbonyl absorption below 6μ.

(b) *Tricresyl phosphate.*—Technical grade (80% *para* and 20% *meta* isomers), represented by Fig. 10. The spectrum of an *n*-butyl phthalate-tricresyl phosphate mixture is given by Fig. 11. This spectrum can easily be interpreted as a composite of the widely differing individual spectra of the phthalate and phosphate.

The weak C—H absorption maximum at 3.5μ, the absorption between 6 and 7μ, and that beyond 12μ strongly suggest the aromatic character of tricresyl phosphate. The strongest absorption maximum, however, occurs between 10 and 11μ and is attributed to the phosphate radical.

Spectrophotometric Determination of Solvent and Camphor

12 *Apparatus*

(a) *Vacuum distillation apparatus.*—See Fig. 12. **A**: Round-bottom flask with 24/40 ⅋ female joint. **B**: Reducer adapter, male joint 24/40 ⅋ to female joint 12/30 ⅋ . **C**: Glass tube, 6 mm i.d. by 12 cm long with 12/30 ⅋ male joint. **D**,**D'**,**D''**: Heavy rubber tubing connections. **E**: Glass tube 6 mm i.d. by 105 cm long, bent approximately as follows: at 20 cm from one end a bend a little less than 90°; at 38 cm from other end a bend a little more than 90°. **F**: Glass tube, 6 mm i.d. by 18 cm long. **G**: Rubber stopper. **H**: Trap constructed from Pyrex test tube, 2.1 cm i.d. by 20 cm long. Side-arm is glass tube 4 mm i.d. by 4 cm, located 3.5 cm from top of tube. The inner shield is a glass tube 18 mm o.d. by 12 cm long fused to a glass tube 6 mm i.d. by 7 cm long. The rubber stopper **G** anchors the shield in the tube.

(b) *Spectrophotometers.*—Cary recording spectrophotometer, Model 14, and Perkin-Elmer recording infrared spectrophotometer, Model 21.

13 *Isolation of Solvent and Camphor*

Assemble the trap **H**, stopper the open ends with rubber policemen, suspend it from the balance pan with a copper wire, and weigh. Immerse the tared trap up to the side arm in

[5] Monsanto Chemical Co., St. Louis, Mo.

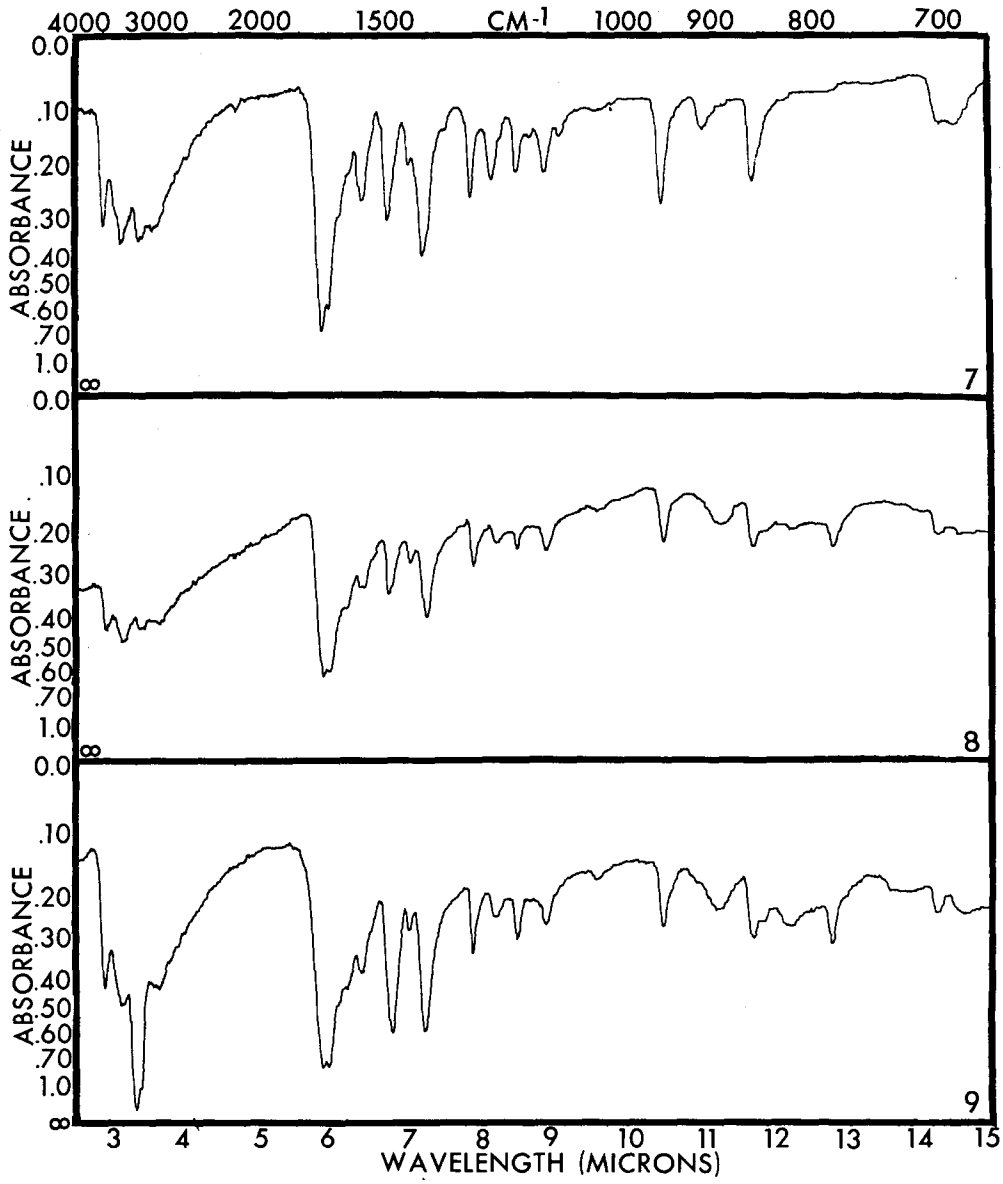


Fig. 7 —Infrared spectrum of a film of guanine derived from commercial nail lacquer.
Fig. 8 —Infrared spectrum of a film of guanine.
Fig. 9 —Infrared spectrum of a mineral oil mull of guanine.

a Dewar flask containing Dry Ice and acetone as a cooling mixture.

Add 5 ml of dibutyl phthalate and a few carborundum chips to the 50 ml round-bottom flask **A**, stopper, and weigh. Remove and discard the brush from the bottle top of the nail lacquer sample. Pour 5–9 g of the nail lacquer into the tared flask and weigh the flask again to determine the sample weight.

Remove and reserve the rubber policemen from the trap. Assemble the apparatus as shown in Fig. 12. Place an ice bath around the flask **A** for several minutes, remove the bath, and apply a vacuum of 1–2 mm or less.

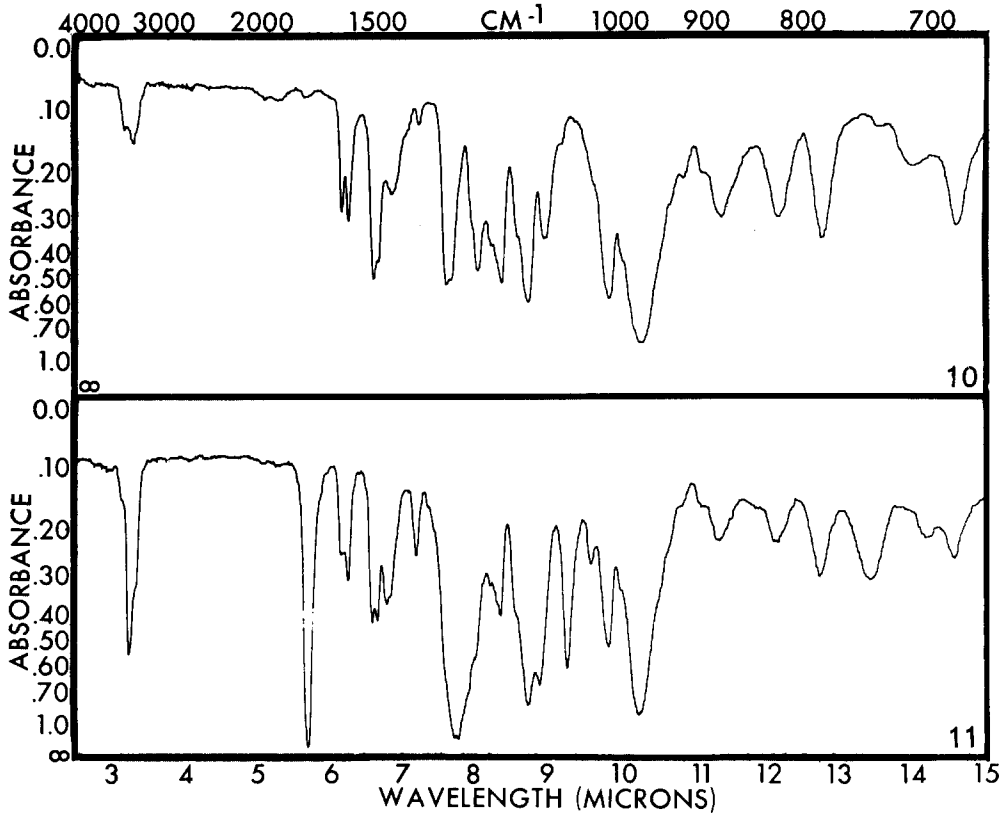


Fig. 10 —Infrared spectrum of a film of technical tricresyl phosphate (80% *para*, 20% *meta*).
Fig. 11 —Infrared spectrum of a film of phthalate-phosphate mixture derived from commercial nail lacquer.

After the initial boiling has subsided, surround the flask with a silicone oil bath, and gradually heat the bath to 125–130°C with a hot plate. Maintain the vacuum and bath temperature for 1 hour. Disconnect the trap, attach the reserved rubber policemen, remove the trap from the Dewar flask, and let it warm to room temperature. Weigh the trap again to determine the weight of solvent and camphor.

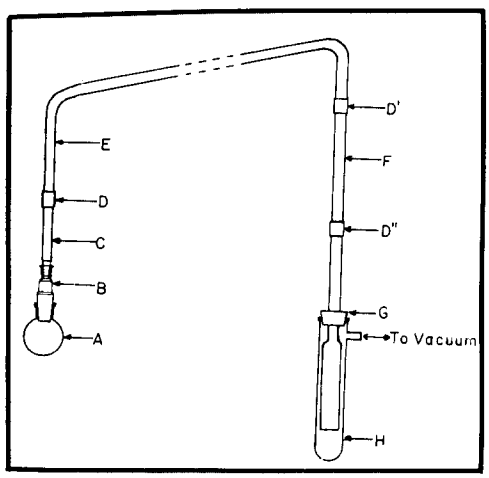


Fig. 12—Vacuum distillation apparatus (not drawn to scale).

Remove the rubber policemen from the trap, take out the inner shield, and invert it over a 25 ml glass-stoppered flask. Pour the contents of the trap through the shield used as a funnel. Stopper and reserve the flask.

14 Determination of Solvent and Camphor

Make an approximate determination of the camphor: Dilute 1 ml of the distillate to 10 ml with ethanol and obtain its ultraviolet spectrum beyond 280 mμ. Use a straight line background correction and calculate the camphor from the absorbance at 300 mμ.

Dilute 1 ml of distillate to 100 ml with CS_2,

obtain its infrared spectrum in the 2–15μ region, and use these data to determine the qualitative composition of the sample. (If the absorbance peaks cannot be attributed to known solvents, repeat the vacuum distillation with a 14–15 g sample, substituting a 100 ml round-bottom flask for the 50 ml one. Arbitrarily fractionate the distillate into several fractions and, as before, examine the infrared spectra of these fractions for qualitative analysis of the substances present.)

Dilute 2.5 ml of the distillate to 50 ml with CCl_4 in a volumetric flask. Add 0.5 g of anhydrous copper sulfate and shake vigorously for 5 minutes to remove any water. Add another 0.25 g of copper sulfate and shake for another 5 minutes. Filter through a fluted filter paper into a flask.

Using the qualitative data obtained from the infrared spectra of the distillate, determine the quantitative composition of the CCl_4 solution spectrophotometrically in the near infrared (1200–2400 mμ).

Prepare standards of the following composition:

	Vol. % in CCl_4
Ethyl acetate	2.5
Butyl acetate	5.0
Toluene	5.0
Commercial xylene	5.0
Ethanol	1.0
Isopropanol	1.0
Butanol	1.0
Camphor (weight %)	5.0

Use the following wavelengths to determine the solvents:

Ethyl acetate	2259.1 mμ
Butyl acetate	2380 mμ
Toluene	2166.5 mμ
Commercial xylene	2172.5 mμ
Ethanol	1412.3 mμ
Isopropanol	1412.3 mμ
Butanol	1412.3 mμ

Measure the absorbances of the sample and of the standard solutions of the solvents present in 1 cm cells at suitable wavelengths. Correct the absorbances of the unknown for the camphor present and calculate the volume per cent composition of the unknown solution by the method of successive approximations or the use of simultaneous equations.

Prepare a solution corresponding to the calculated composition; obtain its infrared spectrum in CS_2 solution and its near infrared spectrum in CCl_4; and compare with the corresponding spectra of the distilled solvent. (In a good analysis they are essentially identical.)

When two or more alcohols are present they can be identified in the 1.4μ region. However, to observe the differences in the spectra of the various alcohols at 1.4μ it is necessary to scan the wavelength slowly and spread the 1.3–1.5μ region on the chart.

Ethanol, isopropanol, and butanol, when present together, can be determined spectrophotometrically by the variable reference titration technique.[6] Suitable wavelengths for the titration are 1.4 and 2.05μ.

15 Determination of Camphor

Weigh about a 4 g sample of nail lacquer into a 500 ml flask, dilute with 10 ml of methanol, and slowly add 225 ml of water with shaking. Connect the flask to a vertical straight-wall condenser through a Kjeldahl trap. Make all connections with ground glass joints. Distill and collect 210 ml of distillate in an ice-cooled flask. Rinse the condenser with 10 ml of methanol and add the rinsing to the distillate. Discard the residue. Acidify the distillate with HCl and extract with several portions of iso-octane (spectrophotometric grade) totaling 100 ml. Discard the aqueous solution.

Filter the iso-octane extracts through a small cotton plug into a 250 ml round-bottom flask with a 24/40 $\overline{\S}$ female joint. Connect the flask to the trap and condenser used for the steam distillation and distill exactly 80 ml at a moderate rate. Reserve the distillate.

Distill the residue in a flask under vacuum as described in **7.12–7.13**, omitting the addition of dibutyl phthalate, and keeping the flask at 100–110°C. After the camphor distills, transfer the contents of the trap to a 100 ml volumetric flask with the aid of iso-octane. Dilute the flask to the mark with iso-octane, mix well, and pour the solution through an Al_2O_3 chromatograph column 7″ long by ⅝″ diameter. Follow with 100 ml of iso-octane, and collect and reserve the last 25 ml of the wash solution. Strip the camphor from the column with 100 ml of chloroform and collect the eluate in a 100 ml volumetric flask. Wash the column with an additional 25 ml of chloroform. Collect and reserve this washing in a separate container. Dilute the camphor solution in the 100 ml volumetric flask to the mark with chloroform and mix well.

[6] *J. Assoc. Offic. Agr. Chemists*, **34**, 135 (1951).

Obtain the ultraviolet spectrum of the camphor solution in a 1 cm cell and determine the camphor from the absorbance at 295 mμ. (In very dilute camphor solutions, a trace of distilled dibutyl phthalate may distort the camphor curve. If this occurs, calculate the camphor from the absorbance at 295 mμ, as before, and then obtain the ultraviolet spectrum of the sample *versus* a chloroform solution containing the calculated amount of camphor. The resultant absorbance difference curve should be similar to that of dibutyl phthalate, if this is the impurity.)

Obtain and examine the ultraviolet curves of the following reserved solutions to check the absence of camphor: the 80 ml distilled iso-octane, the 25 ml wash iso-octane, and the 25 ml wash chloroform.

16 Discussion of Procedure[7]

The solvent composition is determined in terms of volume per cent because it facilitates the preparation of the standard solutions.

With the exception of the alcohols, the infrared spectra are more helpful than the near infrared spectra for qualitative analysis; this situation is reversed for quantitative determinations. The near infrared spectra of the solvents have many well defined absorption peaks. It is more convenient to work with quartz cells and carbon tetrachloride as the solvent than with the customary techniques used to obtain spectra at longer wavelengths.

The camphor values obtained from the procedure of **7.14** are calculated from spectra which have high backgrounds. The spectra cannot be specifically identified as camphor. In the alternative procedure, **7.15**, not only is the background negligible at 295 mμ but the absorbance spectrum identifies the camphor. However, results from the two methods agree reasonably well. On analysis, the camphor content of several commercial nail lacquers was found to be between 1 and 3%.

Determination of Solvents by Gas Chromatography[8]

17 Apparatus

Since so many forms of apparatus are available, a description of the technique used in our laboratories will be given, rather than detailed directions. The path of the eluting gas (helium or nitrogen) through the apparatus was as follows: the pressure regulator; the flowmeter; the copper tube preheater; the reference side of the thermal conductivity cell; the sample inlet; the column; the sample side of the thermal conductivity cell.

The detector was a Gow-Mac thermal conductivity cell (Model NRL (stainless steel) Filament M/T Gas Train double pass, 2 ml) controlled by a Gow-Mac power supply (Model No. 9293). The detector was operated at 140 milliamperes. The recorder was a Varian Associates Graphic Recorder G-10 (10 millivolts).

The preheater and column were housed in an ordinary laboratory oven which could be regulated to ± 2°C. The thermal conductivity cell was mounted outside the oven (its temperature was about 40°C).

18 Determination

Pack soft copper tubing, 4′ long by ¼″ o.d., with 10 g of 30–60 mesh C-22 firebrick impregnated with 4 g of dioctyl phthalate. Assemble the apparatus as described in **7.17**.

Regulate the oven temperature to 75°C and adjust the gas flow rate to about 25 ml/minute. Wait several minutes for the gas to attain pressure equilibrium within the apparatus. Adjust the controls on the power supply and the recorder to the values used in the calibration runs. Weigh accurately about 0.9 g (1 ml) of *n*-propyl acetate (internal standard) into a weighed lacquer sample of approximately 5 g.

Remove the needle from a ¼ ml tuberculin syringe, draw the prepared lacquer into the barrel, replace the needle, eject any air bubbles, and inject about 0.04 ml of lacquer through the serum cap into the top of the chromatograph column.

Hold the temperature at 75°C until the butyl acetate is eluted; then raise the temperature of the oven as quickly as possible to 115°C without altering the flow of gas. After 1 hour more, remove the strip chart and qualitatively identify the solvent constituents by the retention times.

Compute the area under each curve by multiplying the half-band width by the height of the curve. Compare these areas with that of the *n*-propyl acetate band. Use the data obtained from the chromatography of known mixtures of solvents containing known amounts of *n*-propyl acetate to calculate the quantitative composition of the sample.

[7] The procedure is published in *J. Assoc. Offic. Agr. Chemists*, **41**, 668 (1958).

[8] *J. Assoc. Offic. Agr. Chemists*, **41**, 673 (1958).

19 Discussion of the Procedure

In preliminary experiments, the retention times of ethyl alcohol, isopropyl alcohol, ethyl acetate, *n*-propyl acetate, butyl alcohol, butyl acetate, xylenes, and Cellosolve acetate were observed and conditions were selected that appeared to give adequate separation of the components in a reasonable time. Various known mixtures of one or more of these solvents plus *n*-propyl acetate were then chromatographed to determine the area ratios needed to calculate[9] the quantitative results.

The use of an internal standard makes it unnecessary to know the exact sample size or to exactly control the operating variables. *n*-Propyl acetate was chosen as the internal standard since it is unlikely to be found in nail lacquers; its retention time does not overlap that of any of the other solvents considered; and it is eluted between ethyl acetate and butanol. The operating conditions are not necessarily the optimum ones for any particular solvent but represent a compromise that gave the best over-all results for the materials considered.

A single column may be used for about 20 samples of nail lacquer. Each new column must be individually calibrated with known mixtures. Accurate control of the flow rate seems to be the most critical factor in obtaining consistent results for relative areas. When nitrogen was substituted for helium, the response for a given amount of ethanol was greatly decreased.

If either ethanol or isopropanol is present by itself, the alcohol can be identified by its retention time. Mixtures of these alcohols cannot be resolved under the conditions described and are calculated together. The shape of the curve indicates the presence of a mixture and some estimate can be made of the relative amounts of each. The alcohols, although fairly well separated from ethyl acetate, nevertheless interfere to a small extent with that determination.

Although the chromatographic procedure is not as precise as the spectrophotometric method described in **7.12–7.16**, it is more rapid and in some cases permits individual components of the solvent mixture to be identified more easily. This is particularly true when butyl alcohol and ethyl acetate are present.

---

[9] The calculation is discussed in *Gas Chromatography*, by C. Phillips, Academic Press, Inc., New York, 1956, pp. 63–64.