

veloped for the rapid estimation of compositions of mixtures of acetic acid-acetic anhydride-perchloric acid and acetic acid-water-perchloric acid which occur in various three-component baths used in the practical partial acetylation of cotton. The methods are rapid in operation and seem readily applicable in cotton textile finishing plants where partial acetylation processing is conducted. They have been found satisfactory for control methods in pilot-scale operations.

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## Detection of Urea, Melamine, Isocyanate, and Urethan Resins

### Rapid Group Test for Nitrogen, Silicon, Phosphorus, and Titanium in Coating Materials

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► Specific and simultaneous tests for urea-formaldehyde and melamine-formaldehyde coating resins and a test for isocyanate and urethan are presented, that are applicable to coatings in general. A rapid acid-digestion is described for detection of nitrogen, phosphorus, silicon, and titanium. These methods are useful for qualitative identification of synthetic resins in complex systems.

AN IMPORTANT PHASE of research and development in coating materials is the qualitative identification of synthetic resins in complex systems. Most of the fundamental developments in analysis have been applied in this field. The variety of solvents, stabilizers, cross-linking agents, blends, and copolymers encountered prevents employment of a simple analytical scheme. Many properties or tests, such as solubility, odor, burning rate, acid number, and saponification number, are of little value in testing complex formulations. Group and specific chemical tests are dependable and widely used but very few tests, specific for individual resins, are available for this purpose.

Elemental analysis is usually made for halogens, nitrogen, sulfur, phosphorus, and titanium; group tests include cellulose, carboxylic esters, phenyl groups, acetates, and aldehydes. Specific resins or plasticizers are indicated by tests for rosin, phenol, nitrate, silicon, phthalates, and cumarone. Differentiation of individual resins in a large group such as nitrogen resins is difficult by chemical methods for lack of specific tests, and instrumental or solvent separation methods must be used; the latter can be particularly difficult or time-consuming. Tests that are specific for synthetic resins are most valuable but scarce.

Specific tests for urea- and melamine-formaldehyde coating resins and for isocyanate and urethan are presented that are applicable to coatings in general. A more rapid method for elemental detection of nitrogen (including nitrate nitrogen), phosphorus, silicon, and titanium on the same sample digestion is described. All are relatively rapid tests.

*p*-Dimethylaminobenzaldehyde is used to detect urea-formaldehyde and isocyanate resins but under separate conditions. This reagent develops a

yellow color with  $N=C=O$  groups. Urea resins, when hydrolyzed with mineral acid, release urea which reacts readily with the reagent, but this test is not specific. With unhydrolyzed urea resins the test is not positive. With isocyanate and polyurethan resins which contain  $N=C=O$  groups, the test is positive without prior treatment. In glacial acetic acid the yellow color that forms immediately with the isocyanate resins provides a specific test for their identification. These resins react with polyesters and polyols to form the urethan resins. Even after these reactions, the test is still positive. Blocked isocyanate resins that are non-reactive at room temperature develop color rapidly in this test.

A new application of *p*-dimethylaminobenzaldehyde is its use in a mixture of acetic acid and acetic anhydride (3 to 10), in which only urea resins develop a bright blue color. It is particularly interesting that the color does not develop in either glacial acetic acid or acetic anhydride alone, but develops readily in mixtures of certain proportions when refluxed.

A specific test for the melamine-formaldehyde resins is based on the

unusual property of forming an insoluble condensate in the condenser when refluxed with acetic acid or anhydride. The test is sensitive and small amounts can be detected regardless of the presence of other resins. As the urea resin test is conducted in a mixture of acetic acid and anhydride, the tests for these two resins are made simultaneously. Coatings are available which contain both these resins and they are frequently blended together in modifying alkyds for baking finishes. Extremely small amounts of either resin can be detected in an excess of the other.

A rapid microtechnique was developed for the simultaneous identification of nitrogen, silicon, phosphorus, and titanium in coating vehicles. The sample is prepared for test in about 10 minutes; if the stable reagents are prepared in advance, detection of these elements can be completed in about 15 minutes. Silicon is detected during the acid digestion without resort to reagent. The method may also have quantitative application. This acid digestion procedure for detecting nitrogen has two advantages over the usual sodium fusion. In the latter method nitrates and protein do not always react like other nitrogen compounds to form cyanides, and there is always the risk of volatilization of small amounts of nitrogen before fusion temperature is reached.

#### PROCEDURES

**Group Test for Nitrogen, Silicon, Phosphorus, and Titanium. ACID DIGESTION.** Two drops of the coating vehicle are placed in a 10-ml. Kjeldahl microflask which contains a bumping stone such as a Berl saddle. Then 2 ml. of concentrated sulfuric acid and 1 drop of 60% perchloric acid are added. The flask is clamped to a stand under a hood and heated with a Bunsen burner, gently at first until the boiling point is reached. It is then cooled to room temperature with water after a few minutes of air cooling and 4 additional drops of perchloric acid are added. The flask is wiped dry and the acid boiled gently for 3 to 4 minutes. If a clear, colorless solution results, the digestion is complete. If any char or yellow color remains, it is again cooled to room temperature and the addition of 4 drops of perchloric acid and the 3 to 4 minutes of boiling are repeated. It is then cooled to room temperature and diluted to 100 ml. with water.

**Silicon.** If silicone resins are present, a white precipitate of dehydrated silica separates during the digestion and remains insoluble upon dilution. No other material will separate in this manner from the digestion mixture, and no further identification is necessary.

**Titanium.** To a 25-ml. aliquot 2 drops of 30% hydrogen peroxide are added. In the presence of titanium a distinct yellow color develops.

**Nitrogen.** A 25-ml. aliquot is diluted to 83 ml. and 17 ml. of Nessler's reagent, prepared according to Folin and Wu (1), is added. A yellow color in excess of that produced by a blank indicates the presence of nitrogen.

**Phosphorus.** To a 25-ml. aliquot 2 grams of ammonium nitrate, 5 ml. of dilute nitric acid (about 1 to 1), and 25 ml. of ammonium molybdate solution are added. In the presence of phosphorus a yellow cloud or precipitate usually forms at once. If the sample remains clear, it should either be heated or be allowed to stand at least 30 minutes before discarding and reporting as negative.

In case of doubt the tests for titanium and phosphorus can be repeated on more concentrated solutions by diluting the digested sample to 25 ml. instead of the usual 100 ml. If this is done, silicon will still be recognized, but the higher concentration of sulfuric acid in the lower dilution prevents application of the nitrogen test. Some of the materials tested by this procedure are shown in Table I.

condensation and becomes more visible after the sample has cooled.

**ISOCYANATE AND URETHAN RESINS.** From 2 to 5 drops of the vehicle are dissolved in 5 or 10 ml. of glacial acetic acid without the aid of heat. Approximately 0.1 gram of *p*-dimethylaminobenzaldehyde reagent is added. A bright yellow color develops in a few minutes at room temperature if either of these polymers is present. If solid resins are encountered which do not readily dissolve in acetic acid, a small amount of solvent may be used to effect solution.

#### DISCUSSION

In the absence of urea resins the test mixture develops a yellow color on reflux; this should not be confused with the yellow color formed by the isocyanate resins in the cold. The blue color formed by the urea resins is believed to be a dye of the indigo type. If the urea content is very low, the

Table I. Elemental Group Testing of Some Coating Materials

Material Tested	Nitrogen	Phosphorus	Silicon	Titanium
Butadiene-acrylonitrile copolymer	+	—	—	—
Isocyanate resin	+	—	—	—
Melamine-formaldehyde resin	+	—	—	—
Nitrocellulose lacquer, plasticized with tricresyl phosphate	+	+	—	—
Polyamide resin	+	—	—	—
Silicone alkyd enamel	—	—	+	—
Tetraisopropyl titanate	—	—	—	+
Tricresyl phosphate	—	+	—	—
Tris- $\beta$ -chloroethyl phosphate	—	+	—	—
Urea-formaldehyde resin	+	—	—	—
Nondrying oil phthalate alkyd cross linked with 2% tetraisopropyl titanate	—	—	—	+

**Detection of Resins. UREA-FORMALDEHYDE.** A mixture of acetic acid and anhydride can be prepared in advance and stored indefinitely in a glass-stoppered bottle. The optimum ratio is 3 volumes of acetic acid to 10 volumes of acetic anhydride. From 2 to 5 drops of the coating vehicle are placed in a 50-ml., round-bottomed flask having a standard 24/40 ground joint. A bumping stone such as a Berl saddle is added with 10 ml. of the acetic acid-anhydride mixture. Exactly 0.015 gram of *p*-dimethylaminobenzaldehyde powder is added and an air condenser is attached. The flask is placed on an electric heater and the temperature increased until the sample refluxes and the vapors condense in the lower few inches of the condenser. Reflux is continued for 10 minutes. If urea resin is present, a clear blue or blue-green color develops in the flask.

**MELAMINE-FORMALDEHYDE.** During the test for urea resins, if melamine is present, an insoluble white residue collects in the condenser at the point of

yellow color of the blank may be visible with the blue and the resulting color will appear green.

The insoluble residue that condenses to identify the melamine resin is soluble in aqueous alkali, which is recommended to clean the condenser. The ultraviolet and infrared spectra of the residue indicate that it is neither melamine nor melamine-formaldehyde. Ether, secondary amine, and ethylenic linkages are present. The composition of the residue is variable and appears to be due to recondensation of the products of decomposition.

All of the common coating resins have been tested by the procedures for urea, melamine, and isocyanate resins. The only interference noted was from a few of the heat reactive phenolic resins which tend to form a slight blue color in the urea procedure, but the color is a little different and observation of both will allow differentiation.

In the sulfuric acid digestion for the elemental group test, 30% hydrogen peroxide may be substituted for the perchloric acid if desired, using 3 drops of the peroxide for each addition and repeating the cooling and digestion until clear, colorless solutions are obtained. However, this increases the

digestion time to approximately 15 minutes. The perchloric acid is more effective for rapid digestion and is non-hazardous under the test conditions described. The use of perchloric with sulfuric acid for quantitative micro-determination of nitrogen has been reported (2).

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# Detection of Pyrene, Benzo[a]pyrene, and Other Polynuclear Hydrocarbons

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► A new color test has been developed for the detection of polynuclear compounds. A brilliant dark blue color was obtained with pyrene and benzo[a]pyrene. Some eight compounds gave red to violet colors. About 15 other hydrocarbons gave an essentially negative reaction.

THE polynuclear compounds found in the atmosphere include anthracene (1, 2), fluoranthene (1, 2, 12), pyrene (1, 2, 7, 12), alkylpyrene (?) (1), chrysene (7, 12), benz[a]anthracene (12), perylene (1), benzo[a]pyrene (1, 2, 7), benzo[e]pyrene (1, 7), benzo[ghi]perylene (1, 2, 7), and anthanthrene (1). Many of these compounds, as well as coronene, have been found in gasoline engine exhausts (8). Anthracene (3), acenaphthylene (3), pyrene (3, 10), benzo[a]pyrene (3, 10), benz[a]anthracene (9), azulene (10), benzo(e)pyrene (9,10), and a probable alkyl benzo[a]pyrene (10) are stated to be present in tobacco smoke. A few of these compounds or their methyl derivatives cause cancer in mammals (4).

The accelerating growth of industry is linked with increased air pollution. Increasing pollution of the air with cancer-causing chemicals is believed to be one of the dominant agents etiologically associated with the rise in lung cancer deaths (6, 13). Thus, detection of carcinogens in the air is of extreme importance.

#### SPECIAL REAGENTS

Dimethylformamide.  
Tetraethylammonium hydroxide, 10% aqueous solution.

#### EXPERIMENTAL

**Color Test Procedure.** A drop of the test solution containing 5 to 100

γ of the hydrocarbon, fluorenone or quinone in chloroform was evaporated to dryness in a 1-ml. test tube, and 0.1 ml. of fuming nitric acid (density 1.5)-acetic acid (1 to 1) was added. The mixture was heated in a steam bath for 5 minutes and then evaporated to dryness under a vacuum in the steam bath. The residue was dissolved in 0.5 ml. of dimethylformamide, allowed to stand for 30 minutes, and then treated with 0.005 ml. of 10% aqueous tetraethylammonium hydroxide (Table I). For larger quantities of fluorenone or quinone, the volumes of reagents were proportionally increased. In all cases blank solutions containing evaporated chloroform treated with nitric-acetic acid gave negative color reactions with the test procedure.

#### DISCUSSION

**Color Test.** Proof of structure of the hydrocarbons found in the air is based on the similarity of the ultraviolet absorption spectra and/or the fluorescence spectra of the chromatographically separated unknowns to the analogous spectra of known hydrocarbons. As this proof of structure is not unequivocal, other methods need to be developed as supplementary tools for the identification of polynuclear compounds.

Nitrated polynuclear compounds form colored salts containing a resonating negative charge in alkaline solution. In most cases the color involves an an-

Table I. Color Reaction of Some Polynuclear Compounds

Compound	Color	$\lambda_{\max}$ , $M\mu$
Benzo[a]pyrene	Dark blue	622
Pyrene	Dark blue	627
Fluorenone	Red	515
9-Fluorenone	Violet	530
11 H-Benzo[b]fluorene	Violet	520
Triphenylene	Brown-red	500
Benzene	Pink	510
Biphenyl	Light violet	540
p-Terphenyl	Pink	525 <sup>a</sup>
Naphthalene	Pink	475
Anthracene	Brown-red	500
Naphthacene	Light red-blue	460, 590
Phenanthrene	Yellow	...
9,10-Phenanthrenedione	Violet	525
Benz[a]anthracene	Yellow	...
3-Methylcholanthrene	Brown-yellow	...
Chrysene	Dark violet	555
Benzo[c]phenanthrene	Yellow-brown	...
Fluoranthene	Violet	520
Acenaphthene	Brown	465
Dibenzo[a,h]anthracene	Brown-yellow	...
Coronene	Light brown-violet	535
Picene	Brown-yellow	...
Indene	Yellow-brown	...
1,1'-Binaphthyl	Yellow	...

<sup>a</sup> Underlined values are shoulders.