

titration values of 20.79 and 20.76 ml. (20.84 theoretical) for the permanganate and 4.93 and 4.93 ml. (4.86 theoretical) for the copper, respectively. The sum of the two, determined as above or directly, is in good agreement with the theoretical.

The authors have investigated the source of the error and found that, while neither manganous nor citrate ions affect the titer of an iodine solution, the two together cause a noticeable decrease. A small amount of the manganous citrate complex is evidently oxidized by iodine to the manganic complex, which is unstable in the presence of mineral acids. Attempts at substantially increasing the accuracy of the method by variation of the conditions were unsuccessful. Therefore, the authors recommend that the sum of the two oxidants be determined (3) and the copper estimated in a separate sample. This is easily accomplished if the permanganate is first reduced in acid medium by dropwise addition of saturated ferrous ammonium sulfate solution and any excess of the latter is removed by boiling with a little bromine water. Copper is then determined by the method of Park (2), in which interference from iron is prevented by the

addition of fluoride. The accuracy of this procedure is indicated by the following results: Copper was determined in mixtures of 20 ml. of 0.1 *N* copper sulfate and 20 ml. of 0.1 *N* potassium permanganate; the titration values were 20.17, 20.19, and 20.16 ml. of thiosulfate, the theoretical being 20.19, indicating an average error of less than 0.1%. For a direct, accurate determination of small amounts of permanganate in the presence of copper, the method of Swift and Lee is probably the most convenient.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Kapur, R. L., and Verma, M. R., *IND. ENG. CHEM., ANAL. ED.*, **13**, 338 (1941).
- (2) Park, B., *Ibid.*, **3**, 77 (1931).
- (3) Swift, E. H., and Lee, T. L., *Ibid.*, **14**, 466 (1942).

Cupriethylene Diamine as a Solvent for Precise Determination of Cellulose Viscosity

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A modification of the tentative standard A.C.S. method for the precise determination of cellulose viscosity has been developed, using a new solvent—cupriethylene diamine.

A TENTATIVE standard method for determining the viscosity of cellulose in cuprammonium hydroxide was presented by the Committee on the Viscosity of Cellulose, Division of Cellulose Chemistry, at the 74th Meeting of the AMERICAN CHEMICAL SOCIETY, September, 1927. This was to a large extent a composite of methods which were in daily use by large manufacturers of cellulose derivatives and was based upon the wealth of experience gained in the research and control laboratories of these organizations.

The present paper has to do with a method involving a new solvent and a different method of manipulation, which is offered as a rapid and precise method of measuring cellulose viscosity.

That cuprammonium hydroxide is by no means the ideal dispersing agent for the determination of cellulose viscosity is evidenced by the many proposals in the literature for the use of other means. A solution of cupriethylene diamine has been suggested. This solvent is easily prepared and adjusted to constant composition, it may be stored under proper conditions at room temperature, and it shows little evidence of spontaneous decomposition over long periods of time. When cellulose is dispersed in cupriethylene diamine solvent, any considerable amount of atmospheric oxygen during the preparation of the dispersion must be avoided, but these dispersions are much less sensitive to the effects of atmospheric oxygen than are dispersions of cellulose in cuprammonium solvent. When cuprammonium is used as a solvent, it is necessary to use extreme caution to prevent the degrading effects of even minute amounts of oxygen while bringing about cellulose dispersion. The tentative A.C.S. method states that hydrogen or nitrogen must be especially purified to free it from traces of oxygen.

In dispersions of cellulose in cupriethylene diamine solvent, ordinary commercial nitrogen containing about 0.5% oxygen may be used with no appreciable effect, provided dispersion is brought about with reasonable rapidity. Furthermore, a cupri-

ethylene diamine solvent 0.5 molar in copper concentration is a much more efficient dispersing agent than any of the standard cuprammonium hydroxide solvents now in use.

Strauss and Levy (2) were the first to describe the successful use of cupriethylene diamine solutions as a solvent in the determination of cellulose viscosity. They pointed out the desirability of using 0.5 molar copper concentrations and gave clear directions for preparing the solvent. As a result, of experience extending over nearly two years, several modifications and refinements of their method have been worked out and standardized.

The evolution of the method for rapid viscosity determination has been covered by the author (1). This paper describes more fully the method used for precise viscosity determinations where a high degree of precision is required and gives details of the present rapid method used as mill control.

Most of the work done in the author's research laboratory has to do with wood cellulose, the viscosity of which, at 1% concentration, is such that the time of fall of the 1/16-inch aluminum sphere in the standard viscometer is between 5 and 30 seconds. Under these conditions there will be no appreciable change in temperature during the time required for the ball to pass between the two etched marks and it is only necessary to determine the temperature immediately after taking the time of fall of the sphere and apply the temperature correction factor. In dealing with high-viscosity pulps where the time of fall of the standard sphere would exceed 30 seconds, it is desirable to bring the contents of the viscometer to 25° C. by means of a constant-temperature water jacket or to run viscosities at lower cellulose concentration. The author hesitates to apply the Farrow and Neale equations for converting viscosities of solutions at lower concentration to the standard 1% concentration because these equations apply only over very narrow limits of concentration.

PRECISE METHOD

An unpressed sheet of pulp is air-dried to the point where it is in moisture equilibrium with the air of the balance room in

which it is weighed. It is then cut into narrow strips approximately 0.3×3.0 cm. and the moisture on the cut-up sample is determined in the usual way, the balance of the sample being placed in an air-tight container while the moisture content is being determined. Two hundred and fifty milligrams of the pulp on an oven-dry basis are weighed and introduced into the solution bottle, 15 ml. of a cupriethylene diamine solution adjusted to 0.167 copper molarity are added, and the pulp sample is thoroughly wetted with this solution. Ten milliliters of the cupriethylene diamine solution, adjusted to 1.000 copper molarity, are then added, the air in the bottle is swept out by a stream of nitrogen, and the bottle is capped and placed in the shaker for 3 minutes. The rest of the determination is carried out by the rapid method which is used as mill control.

In viscosity determinations on cellulose other than wood, the cellulose may be prepared and dried in any convenient form, if it is not too dense to hinder rapid dispersion. Linters and cotton samples may readily be dispersed, but with high-viscosity material several glass beads should be introduced into the solution bottle to aid in the mechanical breaking up of the cellulose.

The viscometer tube described in the previous publication (1) was designed for viscosity determination by the T.A.P.P.I. capillary flow method, but is no longer used for mill control work. At present, the author uses a straight Pyrex tube 1 ± 0.005 cm. in internal diameter, open at both ends and with etched rings 15 or 18 cm. apart, depending upon the conditions of the test. One end of this tube is closed with a rubber stopper. These tubes are much more readily cleaned than those having a capillary at one end.

METHOD FOR RAPID VISCOSITY DETERMINATION

The following standard method for rapid viscosity determination is in daily use in the control laboratory. If all the conditions are faithfully followed, a high degree of accuracy in mill control may be expected. However, for precise work, a sample should be prepared and accurately weighed as described above. The precise modification, if properly carried out, should give results which check within 1%.

PREPARATION OF CUPRIETHYLENE DIAMINE SOLUTION. *Materials and equipment.* Chemically pure copper sulfate crystals, 28% ammonia, 20% sodium hydroxide solution, and technical grade ethylene diamine, approximately 70%. Stock solution bottles, heavy enough to withstand vacuum obtained with water pump and a pressure of 2 pounds per square inch. These bottles are equipped with two-hole rubber stoppers carrying inlet and outlet glass tubes equipped with short lengths of rubber tubing and pinchclamps. The rubber stoppers are wired into the stock solution bottles. A cylinder of nitrogen with suitable pressure-reducing valve which will allow delivery of nitrogen at 2 pounds pressure.

Strauss and Levy (2) have determined the composition of cupriethylene diamine solution and caution that there must be no excess of ethylene diamine exceeding 2 moles of ethylene diamine to 1 mole of copper.

Two hundred and fifty grams of copper sulfate are dissolved in approximately 2 liters of hot distilled water. The solution is heated to boiling and sufficient strong ammonia is added with violent agitation to render the solution faintly alkaline to red litmus paper (about 117 ml. of strong ammonia are required). The bluish-green precipitate of basic copper sulfate is allowed to settle and is washed with hot distilled water by decantation until free from sulfate ions. This will require five or six washings. Cold distilled water is then added to the precipitate to bring the volume up to about 1.5 liters and to this slurry are added 850 ml. of cold 20% sodium hydroxide solution while agitating violently. The light bluish-green precipitate changes to the definitely blue color of cupric hydroxide, and is then washed with cold distilled water by decantation until free of both hydroxyl and sulfate ions.

When precipitating the original copper sulfate solution with ammonia, it is necessary to have the solution at the boiling point in order to get a precipitate of maximum density which can be rapidly and thoroughly washed by decantation. The cupric hydroxide prepared from the original precipitate will also be dense and readily washed free of soluble salts. The washed cupric hydroxide is then made into a thick slurry having a

volume of approximately 500 ml. and transferred to a 1-liter bottle equipped with a rubber stopper carrying two glass tubes, one of which is straight and extends to within approximately 5 cm. of the bottom of the bottle; the other is a right-angle bend which extends just through the rubber stopper. The stopper is wired down and all the air over the slurry in the bottle is removed by exhausting with the vacuum pump and filling with nitrogen at 2 pounds pressure three separate times. After removal of all air a vacuum is drawn on the bottle and 160 ml. of 70% ethylene diamine are introduced, care being taken to allow no air to enter. The reaction between the cupric hydroxide and the ethylene diamine evolves considerable heat at this point. The contents of the bottle are thoroughly shaken several times over the course of an hour and the solution is then allowed to stand for 12 to 16 hours.

From the stock solution prepared as above, two solutions are prepared for dissolving the pulp samples. One is adjusted to 1.000 ± 0.005 molarity with distilled water and stored under an atmosphere of nitrogen. The second solution is made up from the stock solution and distilled water, adjusted to 0.167 molarity, and stored under an atmosphere of nitrogen.

TESTING CUPRIETHYLENE DIAMINE SOLUTION. *Materials required.* A 250-ml. volumetric flask, 25-ml. pipet, 1.000 N hydrochloric acid, and 0.100 N thiosulfate.

Procedure. After allowing the cupric hydroxide sludge to settle, a 25-ml. sample of the supernatant liquid is made up to 250 ml. A 25-ml. aliquot is acidified with 50 ml. of 4 N sulfuric acid, approximately 3 grams of potassium iodide are added, and the solution is titrated with 0.1 N thiosulfate to a starch end point. The milliliters of thiosulfate required multiplied by 0.04 equals the molarity of the solution in copper.

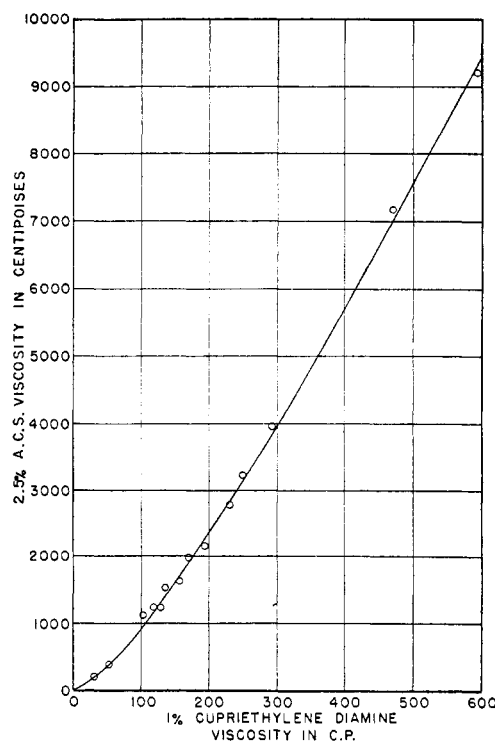
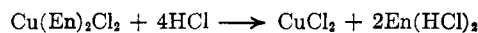


Figure 1

A second 25-ml. aliquot is diluted to approximately 100 ml. with distilled water and titrated with 1 N hydrochloric acid to a faint pink coloration, using 2 drops of methyl orange indicator. The solution changes during this titration from dark blue to light blue and finally develops a pink tinge. The pH of this end point, checked from a large number of samples, is between pH 3.2 and 3.3 as determined with a glass electrode. The milliliters of 1 N hydrochloric acid required multiplied by 0.4 equals the alkalinity of the solution in hydrogen-ion equivalents.

The reactions taking place in neutralization of cupriethylene diamine with hydrochloric acid are:





En = ethylene diamine, $\text{C}_2\text{H}_4(\text{NH}_2)_2$

These reactions indicate a theoretical combination of two ethylene diamine molecules with one of copper.

When an excess of cupric hydroxide is in complete equilibrium with dilute ethylene diamine the actual molar ratio is 1.9 moles of ethylene diamine to one mole of copper, according to the method of testing outlined above.

Viscosity tests of various pulps, using cupriethylene diamine liquors having higher than 2 to 1 ratios of ethylene diamine to copper, have indicated the ratio must be kept below 2.00 to 1 by this test to obtain reproducible viscosities. Viscosities have been shown to be too high by approximately 3 to 5% at a 2.1 to 1 ratio and 25 to 30% at a 3 to 1 ratio.

CALIBRATION OF VISCOSITY TUBES. *Equipment required.* Viscosity tube, 1.00 ± 0.005 cm. inside diameter, 30 cm. long with etched rings 18 cm. apart; $1/16$ -inch aluminum balls, plastic-tipped forceps, accurate thermometer reading to 0.10°C . Constant-temperature bath 25.00°C ., tube holder in bath. Fluorescent light. Standard viscosity oil. Stop watch reading to 0.1 second.

The thermometer, preferably, should have a certified test point at 25.0°C . and the temperature of the bath during calibration should be held as close to this point as possible.

Procedure. The tubes are filled with standard viscosity oil obtained from the National Bureau of Standards. This oil should be between 200 and 300 centipoises at 25°C .; the exact value will be indicated by the Bureau of Standards. The tubes are closed and placed in the constant-temperature bath, held at 25.00°C . for at least an hour before making the determinations. When the tubes have reached constant temperature, a tube is unstoppered and placed in the tube holder in the bath.

The tube holder must hold the tubes in a vertical position, so the falling ball will drop down the center of the tube and not approach the tube wall; otherwise incorrect times of fall will be observed.

Using plastic-tipped forceps, a $1/16$ -inch aluminum ball is carefully dropped in the center of the tube and the time of fall between the etched lines on the tube is determined to the nearest 0.1 second.

The tube factor is calculated as follows:

$$\eta = Kt(D-d)$$

where

- η = viscosity of standard oil at 25°C .
- K = tube and ball constant
- t = time of fall through 18 cm. of standard oil at 25°C .
- D = density of aluminum balls = 2.805
- d = density of standard oil at 25°C .

Then:

$$K = \frac{\eta}{t(D-d)}$$

$$\eta' = t'K(D-d') = t' \frac{\eta(D-d')}{t(D-d)} = t' \frac{1.753\eta}{t(2.805-d)}$$

where

- d' = density of 1% cupriethylene diamine cellulose solution at 25°C . = 1.052
- η' = viscosity of unknown cupriethylene diamine cellulose solution
- t' = time of fall of aluminum ball in unknown solution

PREPARATION OF PULP SAMPLES. *Equipment required.* Centrifuge, 7-cm. Büchner funnel, filter paper, 2 suction flasks, moisture teller, weighing bottles, desiccator, 60-ml. flat medicine bottles with plastic screw caps and rubber gaskets.

Procedure. A sample of the pulp, from a centrifuge pad or a dried sheet, is weighed so as to get from 0.25 to 0.35 gram of oven-dry pulp. The sample is dispersed in approximately 1 liter of water, filtered on a 7-cm. Büchner funnel with filter paper, and washed with two 25-ml. portions of acetone, the acetone being saved for recovery by distillation.

The acetone-washed pulp is stripped from the filter paper and placed in a "moisture teller" with the heat switch on for exactly 2 minutes, then quickly transferred to a tared weighing bottle, and placed in a desiccator until it can be weighed. After the pulp weight is determined, the pulp is transferred to the 60-ml. flat medicine bottle.

The oven-dry content of pulp after 2 minutes' drying in the moisture teller enables one to calculate the amount of the two reagents necessary for dissolving the pulp to give a 1.0% solution.

Tests have shown that when the above equipment and method are used, the pulp will be 99.5% oven-dry.

With different equipment and different pulp, the moisture content of the pulp, after it comes from the moisture teller, may vary from the 99.5% oven-dry which the author has determined. This figure must be determined for each individual mill under actual working conditions.

SOLUTION OF CELLULOSE SAMPLE. *Equipment required.* Shaker, 200 cycles per minute with a 7.5- to 10-cm. amplitude. 1.00 ± 0.005 M cupriethylene diamine, solution B. 0.167 M cupriethylene diamine, solution A. Two 25-ml. pinchcock burets with side tube. Nitrogen cylinder with reducing valve to give 2 pounds pressure.

A table of quantities of solution for weights of samples may be made up according to the oven-dry percentage given by any individual moisture teller by the following formula:

$$0.6 \text{ WB} = \text{ml. of 0.167 cupriethylene diamine}$$

$$0.4 \text{ WB} = \text{ml. of 1.00 cupriethylene diamine}$$

where W = weight of sample and B = % oven-dry.

Procedure. Solution A is added to the bottle from a buret, and the pulp sample is thoroughly wetted. Then solution B is added from a second buret, the bottle is swept out with a stream of nitrogen for at least 15 seconds, and the cap is quickly screwed in place. (The nitrogen is applied to the bottle by means of a 5-mm. glass tube clamped in a vertical position with a rubber tubing connection from the upper end to a nitrogen cylinder with reducing valve which gives approximately 2 pounds per square inch pressure. The 60-ml. bottle is swept free of air by raising it to the glass tube in such a manner that the lower end of the tube extends just below the neck, and the bottle is slowly tipped so as to sweep the nitrogen stream over the surface of the liquid at all corners of the bottle.)

The sample bottle is then shaken by hand or machine for exactly 3 minutes to accomplish solution of the cellulose.

MEASUREMENT OF VISCOSITY IN CENTIPOISES. *Equipment required.* Calibrated viscosity tubes, $1/16$ -inch aluminum balls, viscosity tube viewer with fluorescent light background. Thermometer, reading to 0.1°C . Plastic-tipped forceps for handling aluminum balls.

Procedure. The solution is allowed to stand for exactly 5 minutes to allow escape of any large bubbles entrapped during shaking. Tube is placed in a vertical position so that the standard balls will not approach the sides of the tube as they fall. The time required for a $1/16$ -inch aluminum ball to fall between the 18-cm. marks on the tube is measured with a stop watch.

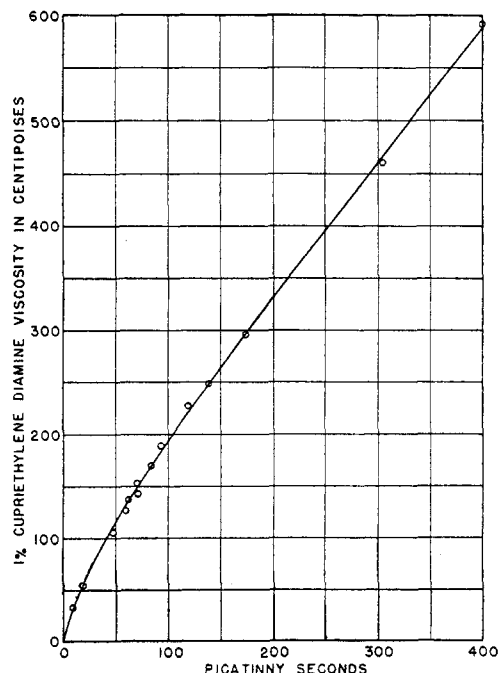


Figure 2

The balls may readily be observed by placing a shielded fluorescent light behind the vertical tube holder. More than one ball should be timed to assure an accurate test.

The temperature of the viscosity solution is measured to the nearest 0.1° C. immediately after determining the falling ball time. It is very important that the temperature of the room be relatively stable so that the temperature of the solution does not change during the time of dropping the balls and measuring the temperature. The viscosity of the solution is determined by the following equation:

$$\text{Log tube constant} + \text{log seconds fall} + (T - 25^\circ \text{C.})(0.01866) = \text{log viscosity at } 25^\circ \text{C.}$$

The temperature correction is added above 25° C. and subtracted below 25° C.

CONCLUSIONS

The author and his assistants developed this method for use in controlling the preparation of pulp to meet viscosity specifications of the Picatinny Arsenal. These specifications follow the tentative standard A.C.S. method, except that viscosity is expressed in seconds of fall of the standard glass sphere through 20 instead of 15 cm., and for pulp to be used in the manufacture of smokeless powder, the time of fall of the standard glass sphere through 20 cm., instead of centipoises, is used to express viscosity.

Figure 1 shows the relationship between parallel determinations made by the tentative standard A.C.S. method using a 2.5% cellulose concentration and the cupriethylene diamine modification using a 1% cellulose concentration.

Figure 2 shows the relationship between parallel tests made according to Picatinny Arsenal specifications and the cupriethylene diamine method using a 1% cellulose concentration.

For very high viscosity it is advisable to use concentrations under 1%, and for very low viscosity to use concentrations above 1%. In order to express the viscosities in terms of 1% concentration, when concentrations above or below 1% are used, it is necessary to determine the mathematical relationship between concentration and viscosity. So far no universal mathematical relationship has been found which may be used to convert viscosities at concentrations above and below 1% to the viscosity at 1% concentration.

LITERATURE CITED

- (1) Hatch, R. S., *Pacific Pulp & Paper Ind.*, p. 13 (Oct., 1942).
- (2) Strauss, F. L., and Levy, R. M., *Paper Trade J.*, 114, No. 3, 31-4 (Jan. 15, 1942).

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Furfural Solution Temperatures of Hydrocarbons Evaluation of Mixed Aniline Point Determination and Application of Furfural

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The application of furfural for the determination of miscibility solution temperatures of petroleum fractions and the influence of the composition of the 60° diluent on the results of the mixed aniline point test have been studied. Furfural offers considerable promise; it is nontoxic and is directly applicable to petroleum fractions of high aromatic content, making possible elimination of mixed aniline point determination.

THE solvency characteristics of various petroleum fractions of the type of solvent oil, solvent naphtha, Diesel fuels, various gas oils, etc., constitute an important index as to the properties such products will display in use. The determination of these characteristics has been an important task of the petroleum technologist, and various methods have been devised for their evaluation. Of these methods, those based upon the miscibility solution temperature of the oil and a solvent liquid are among the most important.

The "miscibility solution temperature" is defined as the minimum equilibrium solution temperature for equal volumes of petroleum product and solvent liquid. Since the different classes of hydrocarbons display different solubilities in various solvents, it is possible to obtain an indication of the nature of an oil from its miscibility solution temperature. Of the various types of solvents proposed for this determination aniline (2) has been the most widely used (6). Nitrobenzene (7), benzyl alcohol (3), ethyl alcohol (4), mixtures of acetone and amyl acetate (14), and nitromethane (8) have also been suggested as solvents for this test.

Aniline appears to have been accepted as the standard solvent in determining miscibility solution temperatures of petroleum fractions; however, it has a number of defects which make it desirable to find a more widely acceptable substitute. Aniline is a blood poison and its fumes are readily absorbed. While indi-

vidual response differs, its high toxicity is generally admitted. Further, aniline cannot be used for the determination of the miscibility temperature of high aromatic content petroleum fractions because of its relatively high freezing point.

In an effort to circumvent this shortcoming, the so-called "mixed aniline point" test has been introduced in relatively recent years in this country as a mode for evaluating these materials. The test represents the minimum, equilibrium solution temperature of a mixture of anhydrous aniline and equal volumes of the material under test and "any naphtha having a straight aniline point of 60° C." (11). It has become increasingly apparent that the results of this test are greatly influenced by the chemical composition of the 60° diluent—i.e., by the aromatic-naphthene-paraffin ratio. As a matter of fact the test, as it is now carried out, is completely meaningless; and it will remain so until the composition of the 60° diluent is standardized or the aniline is replaced by a reagent of lower freezing point. This latter alternative would eliminate the use of a diluent and, hence, the need for standardizing it.

The present paper presents a study of the application of furfural for the determination of miscibility solution temperatures of petroleum fractions. A critical study has been made of the influence of the composition of the 60° diluent on the results of the mixed aniline point test.

Manley, McCarty, and Gross (9) in 1933 studied the use of furfural for the solvent extraction of motor oils. They found it to have a high degree of selective solvent action on a wide variety of petroleum fractions, to be stable in closed systems, possessed of a high application temperature (149° C.), and nonpoisonous. Syono (12) determined the furfural miscibility temperatures of a gasoline of 53.8% aromatic hydrocarbon content at various ratios of furfural to test oil. Trimble (13) recently has studied the solvent properties of furfural, chiefly with inorganic materials, although he tested a number of organic compounds including a solvent naphtha. He suggested that furfural could be used to