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SOLVENCY RATING OF PETROLEUM SOLVENTS BY
REVERSE THIN-LAYER CHROMATOGRAPHY

George G. Esposito

Coating and Chemical Laboratory
Aberdeen Proving Ground, Maryland

November 1972

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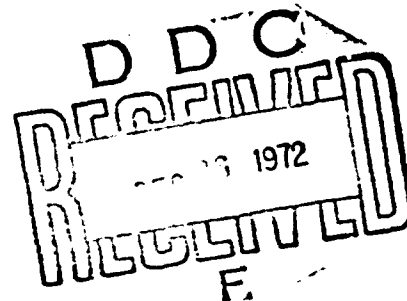
FINAL REPORT

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This report describes a new procedure for evaluating the solvency characteristics of petroleum hydrocarbons that are used as solvents and thinners in organic coatings. The method makes use of the principles and practices of thin-layer chromatography and includes a novel change in normal TLC operating procedure

A standard dye is "spotted" on a glass microber sheet and the edge of the sheet is placed in the solvent to be analyzed. After the solvent has migrated to near the top of the sheet, the sheet is removed, dried, and a ratio of the distances traveled by the dye and solvent is established (R_f value). The R_f value of different solvents is related to their solvent power.

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I. INTRODUCTION

Fundamentally, organic coatings are complex mixtures consisting of solvents, pigments, and binder. The primary function of the solvent is to dissolve or disperse the binder into a stable single-phase system which, after the addition of pigment, can be readily applied on surfaces by various application techniques. Obviously, a solvent must be compatible with other components in a coating system and in addition, it must possess physical and chemical properties that will impart satisfactory viscosity and evaporation characteristics to the coating. The types of solvent used in a paint system are generally dictated by the type of resin required to satisfy a given application. Since a broad spectrum of resins having diverse solubility characteristics are used to formulate different types of organic coatings, it is necessary to select solvents on a rational basis utilizing solvency data obtained from test methods that are capable of measuring their solvent power. The solvency of individual solvents are best defined by the determination of their solubility parameters which are matched with the solubility parameter values of the resin or resins to be dissolved. With petroleum hydrocarbons, solvency is generally determined by measuring their dilution limits relative to a standard material. Established methods for measuring solvency are available, some of which are included in military specifications; however, they do not always provide a true measure of solvent power.

Theory describing the nature of paint resin solutions has been discussed in detail (1) along with test methods for rating solvent power. To have the proper insight into the testing of solvents for solvent power, it is necessary to understand some of the factors affecting the solution of resins. Briefly, hydrogen bonding and other associative forces of coating resins promote the formation of molecular aggregates or clusters of resin molecules that may contain as many as 1,000 molecular units. The extent to which aggregation occurs is dependent upon the type and amount of solvent present in a system. For instance, if a polar solvent is added to a polar resin, such as an alkyd, resin-resin attraction is weakened by the formation of stronger resin-solvent forces. This action causes the solvated resin molecules to disassociate and permits the resin to be solubilized. Conversely, if a nonpolar solvent is added, resin-resin forces are favored over resin-solvent attraction, thereby promoting the formation of resin molecule aggregates. When aggregation reaches sufficient proportions, flocculation or precipitation occurs.

The most significant methods used to obtain solvency data on petroleum solvents are solubility parameter, kauri-butanol (KB) value (2), aniline cloud point (ACP), and dimethyl sulfate value. These methods have been modified and improved over the years and collectively they are capable of yielding considerable information; however each has certain inherent deficiencies which precludes its use as a general procedure. The solubility parameter concept works well for many binary-liquid systems, but it does not relate as well to petroleum solvents which are very complex mixtures of hydrocarbons. KB value measures the ability of a

solvent to keep kauri resin in solution when diluted with butanol. Since kauri resin is natural occurring, great care must be exercised to compensate for variation in composition between different batches. In addition, KB values are not valid when they are related to coating resins having chemical structures that differ greatly from kauri resin. In ACP determinations, the critical solution temperature of a system consisting of aniline and the test solvent is measured. With aliphatic hydrocarbons, equal volumes of solvent and aniline are used. For hydrocarbons high in aromatics, half of the solvent is replaced with n-heptane to keep the solution temperature within a reasonable range; this gives the mixed aniline point. As with KB, solvency is related to a material unlike resins that are to be dissolved and, therefore, it often fails to give an accurate and sensitive measure of solvent power. The dimethyl sulfate value measures the amount of hydrocarbon that is dissolved by the reagent. The method provides a combined percentage of aromatic and olefinic hydrocarbons, but it does not differentiate between the two classes nor does it account for the presence of naphthenes.

This report describes a completely different approach to solvent power evaluation; it makes use of the principles and practices of thin layer chromatography (TLC). In normal TLC operating procedure, a sample is introduced onto a chromatographic plate containing an adsorbent and the plate is placed in a solvent of known composition (mobile phase). Components in the sample are separated according to their differential selective affinities for the adsorbent as they are moved up the plate by the mobile liquid phase. In the new procedure, the operation is reversed. A standard dye is introduced onto a chromatographic plate and the edge of the plate is placed in the sample. As the solvent moves up the plate by capillary action the dye migrates at a rate characteristic of the solvent power of the sample. If the distance traveled by the dye is divided by the distance traveled by the solvent, the R_f value of the dye is obtained; thus, numerical ratings can be assigned to various solvents and solvency data can be compiled.

During the investigation different adsorbent media and various dyes were evaluated. Shamrock Green and Anthraquinone Violet on fiber-glass sheets provided the best distribution of R_f values. Shamrock Green is a mixture of a blue and two yellow dyes; R_f values were determined for the blue dye and the more strongly adsorbed yellow dye. Solvency data are presented for a broad range of hydrocarbon solvents.

II. DETAILS OF TEST

Materials

1. Glass Microfiber, 20 cm X 20 cm sheets. Gelman Instrument Co., Ann Arbor, Michigan.
2. Shamrock Green, Cat. No. A-783, Fisher Scientific, Pitt., PA.
3. Anthraquinone violet, R. Fisher Scientific, Pitt., PA.

Procedure:

Cut the sheets of fiberglass into 5 cm strips and dry at 110°C. Store strips in a dessicator or an oven.

Prepare 0.5% solutions of the dyes in chloroform and apply 5 microliters of each (in parallel) 2 cm from the bottom edge of a microfiber glass sheet. Transfer the sheet (chromatoplate) to a cylinder containing sample, 1 cm deep; attach a tight fitting lid and allow the chromatogram to develop under equilibrated conditions. After the solvent has traveled approximately 18 cm, remove the chromatoplate from the cylinder, mark the solvent front, and allow the solvents to evaporate. Determine R_f values for anthraquinone violet. In addition, compute R_f values for the blue dye and more strongly adsorbed yellow dye in Shamrock Green.

$$R_f \text{ value} = \frac{\text{distance traveled by dye}^*}{\text{distance traveled by solvent}}$$

*Use leading edge of dye as reference point.

Solubility index is determined as follows:

$$\text{Solubility index} = R_f \text{ value} \times 100$$

III. RESULTS

Adsorbent

Of the various adsorbent media investigated, sheets of glass microfiber provided the best overall results. Sheets containing silica, silica gel, and alumina were also evaluated, but the dyes were adsorbed too strongly and did not give good distributions of R_f values.

Dyes

A large collection of dyes were screened according to their solubility in hydrocarbon solvents; those having satisfactory solubility characteristics were then subjected to TLC analysis. Table I shows the R_f values for some dyes; the mobile phases were benzene, cyclohexane, and hexane. Although many of the dyes did not provide a good distribution of R_f values, they did demonstrate a direct solvent polarity - R_f value relationship. Of the dyes tested, Shamrock Green and Anthraquinone violet were selected for further study since they provided the best spread of R_f values. Shamrock Green contains three dyes; the blue dye was used to characterize solvents of low aromaticity and the more strongly adsorbed yellow dye was used for solvents of high aromatic content. Anthraquinone violet was included for solvency index measurements because its R_f values corresponded closely with the blue dye in Shamrock Green, and, as will be discussed later, it can possibly be used alone if proper adjustments are made.

Solvency Index

Table II lists the solvency indices for a group of petroleum hydrocarbons covering a broad range of solvent power. The blue and violet dyes are used for low aromatic types (solubility index below 95), whereas, the yellow dye is used for high aromatic types.

Table II also includes KB values, the most widely used of solubility tests. Except for a few cases, there is good correlation between solvency index and KB value. However, where there is disagreement, solvency index appears to give a better measure of solvent power. For instance, a mixture of 40% toluene and 60% hexane has a KB value of 49, a calculated solubility parameter of 7.75, and a dilution limit (ACP) of only 11.2. The blend is known to be a better solvent than cyclohexane; yet, according to KB, solubility parameter, and ACP the mixture should not be as good as cyclohexane. According to their solvency indices, however, the blend is a better solvent than cyclohexane - solvent blend (yellow dye = 41 and blue dye = 100) and cyclohexane (yellow dye = 7 and blue dye = 41).

Another example where KB and solubility index do not agree is with the solvent tetralin. Tetralin has an exceptionally high KB value of 132, but a more realistic solvency index of 82 (yellow dye).

IV. DISCUSSION

Established methods for the determination of solvent power have been widely used for a number of years; nevertheless, there is need for improvement. The new method appears to fill gaps that exist in older methods. Unfortunately, solvent power is not an absolute measure of the viscosity-reducing ability of hydrocarbons; however, it does provide direction for the selection of a compatible solvent system for an alkyd based organic coating.

In its present form, the method requires at least two dyes to cover the complete range of hydrocarbon paint solvents. Since R_f values for all solvents using a single dye would be simpler to interpret, future studies will be channeled in that direction. Another approach would be to use a single dye, such as anthraquinone violet, which has a limited R_f value range and to expand the range by replacing half the solvent with a nonpolar solvent when solvents of high aromatic content are tested. This approach is analogous to ACP and mixed ACP for low and high aromatic type hydrocarbons.

The concept of reverse TLC is innovative and it should also be useful for the analysis of solvents outside the paint field. The procedure complements other methods for the determination of solvent power, and with additional refinements it could conceivably replace some of the older techniques.

V. REFERENCES

1. Reynolds, W. W., Physical Chemistry of Petroleum Solvents, Reinhold, N.Y , N.Y. (1963).
2. Kiehl, S. R., Am. Paint Varnish Mfgs. Assoc., Circ., 319, 585 (1927).

APPENDIX A

TABLE I

 R_f of Different Dyes on Glass Microfiber Sheets

<u>Dye</u>	<u>Benzene</u>	<u>Cyclohexane</u>	<u>Hexane</u>
Shamrock Green			
Yellow	0.89	0.07	0.05
Blue	1.00	0.45	0.34
Yellow	1.00	0.62	0.55
Anthraquinone Violet	1.00	0.41	0.27
Flamingo Red			
Orange	1.00	0.76	0.70
Red	1.00	0.45	0.32
Perfect Purple	1.00	0.54	0.43
Sunbeam Yellow	1.00	0.71	0.67
Anthraquinone Blue			
Blue	1.00	0.20	0.12
Blue'	1.00	0.38	0.21
Oil Orange	1.00	0.79	0.66
Oil Yellow	1.00	0.78	0.68
Butter Yellow	1.00	1.00	1.00
Anthraquinone Iris			
Red	1.00	0.40	0.11
Blue	1.00	0.36	0.22
Purple	1.00	0.57	0.41

TABLE II
Solvency Indices

Solvent	Solvency Index			K _S Value
	Anthraquinone Violet	Shamrock Yellow	Green Blue	
Benzene	100	89	100	107
Toluene	100	90	100	106
Xylene	100	92	100	99
Tetrafin	100	82	100	132
Aromatic thinner	100	86	100	93
40% toluene, 60% hexane	100 ¹	41	100	49
30% toluene, 70% hexane	95	18	50	41
20% toluene, 80% hexane	82	11	82	36
Cyclohexane	48	7	41	58
Methyl cyclohexane	62	9	63	51
Mineral spirits	38	6	42	33
VH&P naphtha	51	8	48	38