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SUBCOMMITTEE ON ANALYTICAL METHODS

RECOMMENDED METHODS FOR THE ANALYSIS OF ALKYD RESINS

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FOREWORD

This is the second publication of the Subcommittee on Analytical Methods of the Organic Coatings Section, the first being 'Recommended Methods for the Analysis of Drying Oils'. The trend of the Organic Coatings industry has been to use oil-modified resins, particularly alkyd resins, in place of the simpler drying oils and this has brought the need for standard methods for analysis of these resins. The methods chosen for investigation were those considered to be of most importance in current practice.

Of the chemical methods, particular attention has been given to the method for the determination of hydroxyl value, on which there were conflicting views. In a cooperative exercise, laboratories in five countries obtained highly satisfactory results by two methods and since there was little to choose between them both are included.

As envisaged in the earlier publication, increasing use is made of instrumental (chromatographic and spectroscopic) methods. In the present state of development they are of main value for qualitative or semi-quantitative analysis. The gas chromatographic methods were the subject of a further cooperative investigation involving laboratories in five countries.

The methods for the determination of phthalic anhydride content and fatty acids content are essentially equivalent to those of A.S.T.M. D563–52 and D1398–58 respectively.

The members of the Subcommittee who took part in the work were

Dr R. Bult (drs F. H. de la Court)	Netherlands
Dr M. Hochweber	Switzerland
Mr H. K. Raaschou Nielsen	Denmark
Mr P. Fink-Jensen (Mr G. Christensen)	Denmark
Mr B. Hemberg	Sweden
Mr A. Toussaint	Belgium
Dr L. A. O'Neill	Great Britain

Thanks are due to Mr A. Toussaint for providing a French translation and to drs de la Court (T.N.O.) for suggesting the gas chromatographic methods and providing samples for the cooperative investigation.

L. A. O'NEILL
Chairman of the Subcommittee on Analytical Methods

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1. ACID VALUE

1.1 Definition

The acid value is defined as the number of milligrammes of potassium hydroxide required to neutralize one gramme of the sample under the conditions specified below.

1.2 Scope

The acid value is a measure of the free carboxyl groups in the alkyd. Free anhydride groups are also partially measured. The content of anhydride groups in a finished alkyd is likely to be small but in samples of alkyd of high acid value taken in the early stage of reaction it may be appreciable. In this case, the anhydride groups may be determined separately, or the acid and total anhydride groups determined by an alternative procedure in which the latter are fully hydrolysed.

1.3 Reagents

Standard potassium hydroxide solution (0.1N) in methanol.

One per cent of phenolphthalein in ethanol (95 per cent). Other indicators with a colour change in the same pH range (8.3–10) may be used also.

Ethanol–toluene mixture. Equal volumes of ethanol (95 per cent) and toluene are mixed and neutralized with a methanolic potassium hydroxide solution (0.1N) in the presence of phenolphthalein as indicator.

1.4 Procedure

Weigh to the nearest 0.01 g into a conical flask, 1–2 g of the sample, according to the expected acid value.

Add 50 ml of ethanol–toluene mixture to the sample and shake until solution is complete.

Titrate with methanolic potassium hydroxide solution in the presence of phenolphthalein as indicator.

1.5 Calculation

Calculate the acid value as follows:

$$\text{Acid value} = 56.1\ aN/p$$

a = ml methanolic potassium hydroxide solution

N = normality of the methanolic potassium hydroxide solution

p = weight of the sample in g.

2. SAPONIFICATION VALUE

2.1 Definition

The saponification value is defined as the number of milligrammes of potassium hydroxide required for the saponification of one gramme of the sample under the conditions specified below.

2.2 Scope

The saponification value is a measure of the sum of the free and hydrolysable acids in the alkyd. The determination can be carried out on straight

and modified alkyds. For simple alkyds of known type it provides a measure of the oil length.

2.3 Apparatus

Conical flasks of alkali-resistant glass of 200 or 300 ml capacity.

Reflux condensers. The use of interchangeable ground glass joints is recommended.

2.4 Reagents

Standard hydrochloric acid solution (0.5N).

Potassium hydroxide solution (0.5N) in ethanol (95 per cent). This solution must be colourless or not darker than straw yellow.

One per cent of phenolphthalein in ethanol (95 per cent). Other indicators with a colour change in the same pH range may be used also.

2.5 Procedure

Weigh to the nearest 0.001 g into a conical flask, approximately 1 g of the sample; dissolve in 5 ml of toluene.

Add exactly 25 ml of ethanolic potassium hydroxide solution to the solution by means of a burette or another suitable instrument of equal precision, and 5 ml of water. Connect the flask with a condenser and reflux for 1 hour, shaking from time to time.

Titrate the soap solution, while still warm, with hydrochloric acid solution in the presence of phenolphthalein as indicator.

Carry out a blank by refluxing and titrating exactly 25 ml of ethanolic potassium hydroxide solution under the same conditions.

2.6 Calculation

Calculate the saponification value as follows:

$$\text{Saponification value} = 56.1\ (b - a)\ N/p$$

a = ml hydrochloric acid required for the titration of the sample
b = ml hydrochloric acid required for the titration of the blank
N = normality of the hydrochloric acid solution
p = weight of the sample in g.

3. HYDROXYL VALUE

3.1 Definition

The hydroxyl value is defined as the number of milligrammes of potassium hydroxide required to neutralize the acetic acid taken up on acetylation of one gramme of the sample. The hydroxyl content is commonly expressed in these units, in conformity with the acid and saponification values.

For comparison with hydroxyl contents determined by methods other than acetylation, e.g. active hydrogen or infrared spectroscopic methods, the hydroxyl content may be expressed as the percentage of hydroxyl groups, by multiplying the hydroxyl value by the factor 17/560.

3.2 Scope

Determination of the free hydroxyl groups present in the alkyd, these being

present as free polyhydric alcohol, partial esters, polyester end groups or hydroxylated fatty acids. Two equally satisfactory methods are proposed.

3.3 Method 1

3.3.1 Apparatus

Glass-stoppered conical flasks of about 250 ml capacity.

Reflux condensers. The use of ground glass joints is required.

Water bath.

3.3.2 Reagents

Standard potassium hydroxide solution (0.5N) in methanol. Standardize this solution against potassium acid phthalate.

Acetylating reagent. Dissolve 10 ml of redistilled acetic anhydride in 90 ml of redistilled pyridine. Make sure that the titration of 10 ml of this reagent requires a volume between 40 and 50 ml of the methanolic potassium hydroxide solution.

One per cent of phenolphthalein in ethanol (95 per cent).

Potassium acid phthalate, primary standard grade.

Toluene–butanol mixture, 1:2 (v/v). Neutralize this mixture with methanolic potassium hydroxide solution in the presence of phenolphthalein as indicator.

3.3.3 Procedure

Weigh the sample to the nearest 0.001 g into a dry conical flask. The weight of the sample is chosen so that 3.0 to 3.5 milliequivalents of hydroxyl are present; this corresponds in g with 170, divided by the expected hydroxyl value.

Add exactly 10 ml of acetylating reagent by means of a pipette. Connect the flask with a condenser and heat on a boiling water bath for 2 hours, shaking gently in the initial stages of the heating to promote solution of the sample in the reagent.

Add 10 ml of cold distilled water down the condenser and continue the heating for a further 15 minutes.

Cool the flask by immersion in a beaker of cold water and, while immersed, add 75 ml of toluene–butanol mixture down the condenser so as to wash thoroughly the condensing surface of the condenser.

Remove the condenser from the flask and allow the contents of the flask to cool to room temperature.

Titrate with methanolic potassium hydroxide solution in the presence of phenolphthalein as indicator.

Carry out a blank with exactly 10 ml of acetylating reagent under the same conditions.

3.3.4 Calculation

Calculate the hydroxyl value as follows:

$$\text{Hydroxyl value} = \frac{(b - a)\,N \times 56.1}{p} + \text{A.V.}$$

a = ml methanolic potassium hydroxide solution required for the titration of the sample
b = ml methanolic potassium hydroxide solution required for the titration of the blank
N = normality of the methanolic potassium hydroxide solution
p = weight of the sample in g
A.V. = the acid value of the sample.

3.4 Method II

3.4.1 Apparatus

Glass-stoppered conical flasks of about 250 ml capacity.
Bath adjusted at 50°C (± 1°C).

3.4.2 Reagents

Standard potassium hydroxide solution (0.50N) in methanol. Standardize this solution against potassium acid phthalate.

Acetylating reagent. Dissolve 4.0 g of *p*-toluene sulphonic acid ($CH_3C_6H_4SO_3 . H_2O$) in 100 ml of ethyl acetate (dried over barium oxide and distilled), preferably by means of a magnetic stirrer. To this solution, add slowly while stirring 33 ml of distilled acetic anhydride. Make sure that the titration of 5 ml of this reagent requires a volume between 40 and 50 ml of the methanolic potassium hydroxide solution.

One per cent of phenolphthalein in ethanol (95 per cent).

Potassium acid phthalate, primary standard grade.

Toluene–butanol mixture, 1:2 (v/v). Neutralize this mixture with methanolic potassium hydroxide solution in the presence of phenolphthalein as indicator.

Pyridine–water mixture, 3:1 (v/v)

Ethyl acetate (dried over barium oxide and distilled).

3.4.3 Procedure

Weigh the sample to the nearest 0.001 g into a dry conical flask. The weight of the sample is chosen so that 5 to 6 milliequivalents of hydroxyl are present; this corresponds in g with 280, divided by the expected hydroxyl value. However, do not use a sample weight of more than 10 g, as would be the case with resins with hydroxyl value below 28.

Add 5 ml of ethyl acetate and shake, if necessary under gentle warming, until the sample is dissolved.

Allow to cool to room temperature, add exactly 5 ml of acetylating reagent by means of a pipette and stopper the flask.

Place the flask for twenty minutes in a bath adjusted at 50°C (± 1°C) in such a way that the liquid in the flask is just above the level of the liquid in the bath and shake every 5 minutes.

Remove the stopper, add 2 ml of water and shake vigorously.

Add 10 ml of pyridine–water mixture, rinsing the sides of the flask during the addition.

Allow the flask to stand for 5 minutes at room temperature, add 60 ml of toluene–butanol mixture and titrate with methanolic potassium hydroxide solution in the presence of phenolphthalein as indicator.

Carry out a blank with exactly 5 ml of acetylating reagent under the same conditions.

3.4.4 Calculation

See method I.

4. PHTHALIC ANHYDRIDE CONTENT

4.1 Scope

In this method the phthalic anhydride content of alkyd resins including those containing styrene is determined. This method is not applicable for the determination of phthalic anhydride in alkyd resins containing other dibasic acids such as maleic or fumaric, or modifying agents such as urea, melamine, and phenolic resins.

4.2 Apparatus

A 500 ml conical flask fitted with an air-cooled glass reflux condenser 30 in in length.

Water bath.

A sintered glass filter crucible, fine porosity, of 30 ml capacity.

A desiccator containing concentrated H_2SO_4 as the desiccant.

A guard tube filled with soda lime.

Filter flasks.

Crucible holder.

4.3 Reagents

Benzene.

Alcoholic potassium hydroxide solution. Dissolve 66 g of reagent grade KOH in 1 litre of absolute ethyl alcohol (*Note 1*). Allow the solution to stand overnight protected against CO_2 absorption. Filter just before use.

Anhydrous analytical reagent grade ether.

Alcohol–benzene wash solution. One volume of absolute ethyl alcohol is mixed with three volumes of benzene.

Hydrochloric acid (0.1N).

4.4 Procedure

Weigh by difference, from a closed container into the 500 ml conical flask, a sample of resin or resin solution sufficient to yield from 0.8 to 1.2 g of potassium alcohol phthalate. Add 150 ml of benzene, warming slightly on the steam bath, if necessary, to effect solution. Add 60 ml of alcoholic KOH solution, and attach the condenser.

Place the flask in a water bath to a depth approximately equal to that of the contents of the flask. Warm the bath, maintaining a temperature of 40°C for 1 hour, then gradually raise the temperature until the alcoholic solution boils gently. Reflux for $1\frac{1}{2}$ hours.

Remove the flask from the bath and wash down the inside of the condenser with a few millilitres of alcohol–benzene wash solution. Remove the condenser, cap the flask with the soda-lime guard tube, and cool by means of running water or an ice bath.

When cool, filter immediately, and as rapidly as possible, through a sintered glass crucible that previously has been weighed, using the alcohol–benzene wash solution for transferring the precipitate and washing the reaction flask. Wash the precipitate with successive portions of alcohol–benzene wash solution until a few millitres of washings collected in a second suction flask are no longer alkaline to phenolphthalein. (Normally about 75 ml of wash solution are sufficient.) Do not allow air to be drawn through the crystals, as they are hygroscopic. Finally pour 25 ml of ether into the crucible and draw through the precipitate with the aid of suction.

Wipe the outer surface of the crucible with a clean cloth and place in a gravity convection oven at 60°C for 1 hour (*Note 1*).

Cool to room temperature in a desiccator, and weigh.

Note 1

The precipitate is the alcoholate $C_6H_4\ (COOK)_2.(C_2H_5OH)$, and the alcohol of crystallization will be slowly driven off on prolonged heating. It is safe, however, to dry the alcoholate at a temperature up to 60°C for as long as 1 hour.

Correction for carbonate-coprecipitation of K_2CO_3 with the potassium alcohol phthalate may be a source of error. If a correction for K_2CO_3 is desired, proceed as follows:

Dissolve the weighed precipitate in about 50 ml of distilled water that has been neutralized to phenolphthalein. Add 3 to 4 drops of phenolphthalein indicator, and if the solution is alkaline, titrate with 0.1N HCl.

4.5 Calculation

Calculate the percentage of phthalic anhydride in the sample as follows:

$$K = VN \times 0.1382$$

Phthalic anhydride, per cent

$$= \frac{(P - K) \times 0.5136}{S} \times 100$$

K = correction for K_2CO_3, in grammes (if determined)
V = millilitres of HCl used for titration
N = normality of HCl
P = grammes of potassium alcohol phthalate
S = grammes of sample used.

5. FATTY ACIDS CONTENT

5.1 Scope

This method covers the gravimetric determination of the total fatty acid content of alkyd resins free from modifying agents.

5.2 Apparatus

A 500 ml conical flask fitted with an air-cooled glass reflux condenser 30 in in length.

Water bath and steam bath.

A sintered glass filter crucible, fine porosity of 30 ml capacity.
Crucible holder.
A desiccator containing concentrated H_2SO_4 as the desiccant.
A guard tube filled with soda lime.
Filter flasks, filter funnel and filter papers.
Beakers, 150 and 400 ml.
Three 500 ml separating funnels.
Vacuum drying oven.
Nitrogen gas.

5.3 Reagents

Anhydrous sodium sulphate.
Universal indicator paper.
Benzene.
Alcoholic potassium hydroxide solution. Dissolve 66 g of reagent grade KOH in 1 litre of absolute ethyl alcohol (*Note 1*). Allow the solution to stand overnight protected against CO_2 absorption. Filter just before use.
Ether—anhydrous analytical reagent grade ether.
Alcohol–benzene wash solution. Mix one volume of absolute ethyl alcohol with three volumes of benzene.
Hydrochloric acid (sp.gr. = 1.19).

Note 1

The alcohol may be denatured but must be absolute.

5.4 Procedure

Weigh by difference, from a closed container into the 500 ml conical flask, a sample of resin or resin solution sufficient to yield from 0.8 to 1.2 g of potassium alcohol phthalate. Add 150 ml of benzene, warming slightly on the steam bath, if necessary, to effect solution. Add 60 ml of alcoholic KOH solution and attach the condenser.

Place the flask in a water bath to a depth approximately equal to that of the contents of the flask. Warm the bath, maintaining a temperature of 40°C for 1 hour then gradually raise the temperature until the alcoholic solution boils gently. Reflux for $1\frac{1}{2}$ hours.

Remove the flask from the bath, and wash down the inside of the condenser with a few millilitres of alcohol–benzene wash solution. Remove the condenser, cap the flask with the soda-lime guard tube, and cool by means of running water or an ice bath.

When cool, filter immediately, and as rapidly as possible, through a sintered-glass crucible that previously has been weighed, using the alcohol–benzene wash solution for transferring the precipitate and washing the reaction flask. Wash the precipitate with successive portions of alcohol–benzene wash solution until a few millilitres of washings collected in a second suction flask are no longer alkaline to phenolphthalein. (Normally about 75 ml of wash solution are sufficient.) Do not allow air to be drawn through the crystals, as they are hygroscopic. Finally pour 25 ml of ether into the crucible and draw through the precipitate with the aid of suction.

Transfer the combined filtrate and washings to the 400 ml beaker with the aid of 25 ml of water from a wash bottle.

Concentrate on the steam bath to a volume of approximately 25 ml under a blanket of nitrogen to prevent oxidation of the fatty acids using a hood. Transfer to a 500 ml separating funnel with the aid of water from a wash bottle, dilute with water to approximately 300 ml, and add 10 ml of alcohol.

Extract the unsaponifiable and volatile thinners with successive 50 ml portions of ether (not less than three, or until a colourless ether extract is obtained), combining the ether extracts in the first separating funnel and using the other two funnels for the successive extractions (*Note 2*). Finally, wash the combined ether extracts with three 15 ml portions of water, adding the water washes to the main aqueous phase. Discard the combined ether extracts.

Note 2

If the layers do not separate easily, carefully draw off the lower, clear aqueous layer and add 2 to 3 ml of alcohol, by means of a pipette, to the ether emulsion phases in the separating funnel. Swirl gently to break the emulsion, and continue to draw off the lower layer. This procedure for breaking the emulsion may be repeated on subsequent extractions, if necessary.

Acidify the aqueous phase to a pH of approximately 2 by slowly adding HCl, cooling under running tap water. When the mixture has cooled to room temperature, extract the fatty acids with successive 25 ml portions (not less than three) of ether until a colourless ether extract is obtained, combining the ether extracts in the first separating funnel and using the other two funnels for the successive extractions. Wash the combined ether extracts with successive 10 ml portions of water until free of mineral acid when tested with an indicator paper. Discard the aqueous phase.

Dry the combined ether extracts in the separating funnel by the addition of successive small quantities of anhydrous Na_2SO_4.

Note 3

The free water will have been removed when, by the addition of a small quantity of Na_2SO_4 and gentle swirling, the excess Na_2SO_4 will be seen to disperse as a freely moving powder.

Filter the dried ether extract through rapid, low ash paper, portionwise into the 150 ml beaker, containing a small boiling stone and previously weighed to the nearest 1 mg. The ether extract should be decanted from the top opening of the separating funnel. Evaporate the ether portionwise by placing the beaker and its contents on the steam bath, in a hood. Cover the filter funnel with a watch glass during the portionwise evaporation steps and apply a blanket of nitrogen over the beaker during evaporation. Remove the last portions of fatty acids from the Na_2SO_4 by washing with successive small portions of ether until a colourless extract is obtained. Remove the final traces of fatty acids from the filter paper by using several successive small portions of ether.

Complete the evaporation of the fatty acid ether solution on the steam bath, while maintaining a nitrogen atmosphere over the acids. Remove the final traces of ether by heating for successive 20 minute periods in a vacuum oven at 60°C until minimum weight is obtained. After each heating period,

allow the beaker and contents to cool in a desiccator and then weigh to the nearest milligramme.

5.5 Calculation

Calculate the total fatty acids content as follows:

$$\text{Total fatty acids, per cent} = \frac{A - B}{W} \times 100$$

A = weight of beaker plus residue
B = weight of beaker
W = weight of sample taken.

6. IDENTIFICATION OF TYPE OF ALKYD RESIN BY INFRARED SPECTROSCOPY

The infrared spectrum provides information on the type of alkyd resin under examination. The main constituents from which the resin is made and any modifying agents can often be recognized. The evidence depends on the presence and intensity of particular bands in the spectrum. In some cases, the bands are sufficiently characteristic to enable components to be identified with certainty; in others the interpretation is more doubtful, and the bands for some modifying agents may be masked by those of the parent alkyd.

In some cases, where the nature of the components of the alkyd resin are known, quantitative estimations of oil length or of the proportion of modifying agents may be made.

6.1 Preparation of sample

The spectrum of the alkyd resin may be obtained by any of the standard methods of infrared spectroscopy. The simplest method is to examine the resin in film form; for a liquid resin this can be done by pressing the sample between two sodium chloride plates and for a solid by evaporation from solution on to a sodium chloride plate or potassium bromide disc (taking care to remove residual solvent under vacuum or in a current of inert gas at 50°C).

The resin may also be examined in solution (in a solvent, the spectrum of which causes minimum interference, such as CS_2 or CCl_4), as a mull with an inert liquid (liquid paraffin or a fluorinated hydrocarbon), or as a pressed disc with inorganic powder (potassium bromide).

If a wedge-shaped film of the sample is prepared this facilitates the choice of the most suitable film thickness.

In all cases resin films should be compared among themselves or with known standards at similar film thicknesses.

These procedures will give the spectrum of the original alkyd, but if the alkyd is of an oxidizing type and the film is allowed to dry in air, chemical changes occur and the spectrum alters. Account must be taken of this in comparing the spectrum of a dried alkyd film with that of the original alkyd.

A special technique for obtaining the spectrum of a film already attached

to a substrate is by attenuated total reflectance (a.t.r.) spectroscopy. In interpretation it must be remembered that the spectrum obtained is that of the upper layers of the film only and there are small differences between the spectra obtained by a.t.r. and transmission methods.

6.2 Interpretation of spectra

The spectrum obtained will show general features characteristic of most alkyd resins and special features which assist in the identification of particular components.

The general bands are in the following regions:

Band region (μm)	*Causative group*
2.8 to 2·95	Hydroxyl
3.3 to 3.4	Hydrocarbon
5.7 to 5.9	Ester and acid
6 to 6.75	Aromatic ring
6.75 to 7.5	Aliphatic hydrocarbon
7.5 to 10	Ester
10 to 10.5	*Trans* unsaturation
10.5 to 14·5	Aromatic ring

The extent to which particular bands give an indication of particular components is considered below for each group, namely polybasic acids, monobasic acids, polyhydric alcohols and modifying agents.

6.3 Polybasic acids

Clear distinction can be made between *o*-phthalic and isophthalic acid groups from the following bands:

o-phthalic 6.2, 6.3, 7.9, 8.9, 9.3, 13.5, 14.2 μm
isophthalic 6.2, 7.7, 8.2, 8.6, 9.1, 13.7 μm

Indications of the presence of other polybasic acids can sometimes be obtained by the band pattern in certain regions. Thus trimellitic anhydride gives a band at 12.6 μm.

No bands generally reliable for the recognition of maleic anhydride modification of an alkyd have been found, but bands at 3.1, 6.05 and 12.9 μm are sometimes indicative. Free anhydride groups, whether from residual phthalic anhydride or maleic anhydride give bands at 5.4 and 5.65 μm.

6.4 Monobasic acids

The different fatty acids in an alkyd resin cannot readily be distinguished from the infrared spectra. The most useful region is 10 to 10.5 μm which is indicative of *trans* unsaturation. This can be characteristic for tung oil or dehydrated castor oil but for non-conjugated natural oils, such as linseed or soya, it indicates only *trans* unsaturation developed during the resin manufacture.

In this region, unsaturated oils of this type will show a band at 10.3 μm characteristic of monoene or non-conjugated *trans* unsaturation.

Tung oil and dehydrated castor oil acids will however show bands of conjugated *trans* unsaturation at 10.1 μm.

In alkyds based on saturated fatty acids these *trans* bands will be completely absent.

Oils of hydroxylated fatty acids (castor oil) will show a strong hydroxyl band at 2.9 μm but this is not distinguishable from that due to the unesterified hydroxyls of the polyhydric alcohol. Of other monobasic acids, benzoic acid, in conjunction with *o*-phthalic acid, gives a band at 14.05 μm compared to one at 14.2 μm in the presence of the *o*-phthalic acid alone and also at 9.7 μm.

6.5 Polyhydric alcohols

Assistance in the recognition of the polyhydric alcohol component is sometimes obtained from the i.r. spectrum.

Glycerol may often be distinguished from trimethylol ethane (TME), trimethylol propane (TMP), pentaerythritol and mixtures of these polyols with glycerol, by the shape of the band at 7.25 μm. This is sharp and very small with glycerol, but broader when pentaerythritol is present and considerably longer when trimethylol ethane and trimethylol propane (TME and TMP) are present.

Furthermore, in spectra of alkyds containing pentaerythritol, TMP and TME the CH_2-bands and CH_3-bands at 6.9 μm have been shifted towards lower wavelengths with the result that the benzene ring at 6.7 μm, which is shown as a distinct sharp peak in the spectrum of the glycerol alkyd, appears only as a shoulder in the spectra of pentaerythritol, TMP and TME.

Finally, the spectrum of a glycerol esterified alkyd is characterized by an absorption at 9.1 μm (which partly eliminates the minimum at 9.15 μm) which is characteristic of spectra of alkyds containing pentaerythritol, TMP and TME.

When mixtures of glycerol and pentaerythritol are present in alkyds the spectra are difficult or impossible to distinguish from spectra of alkyds containing pentaerythritol as the only polyol.

6.6 Modifying agents

Modification of the alkyd with styrene or vinyltoluene can be recognized. In *o*-phthalic based alkyds styrene causes a shift of the 14.2 μm band to 14.3 μm with increase of intensity; the band at 6.2 μm becomes stronger than the 6.3 μm band, instead of weaker as in unmodified alkyds; vinyltoluene also increases the intensity of the 14.2 μm band and gives a band at 12.8 μm. New bands are introduced at 8.6 μm and 12.3 μm.

Modifications with rosin or with phenolic resin do not cause specific changes in the spectrum, to enable their recognition.

Modifications with acrylate or methacrylate esters may sometimes be recognized by bands at 8.3, 8.7 and 10.1 μm.

The presence of urea–formaldehyde condensate in an alkyd resin can be detected by a band at 6.1 μm and of melamine formaldehyde by a sharp band at 12.25 μm.

Silicone modified alkyds show a broad absorption at 8.5 to 10 μm.

6.7 Quantitative analysis

An estimation of the oil length of the alkyd may be obtained by determining

the ratio:

$$\frac{\text{C—H absorbance at 3.4 μm}}{\text{C=O absorbance at 5.75 μm}}$$

and reading the oil length from a calibration graph. Results are more accurate if a graph specific for the type of oil in the alkyd is used.

Estimation of the styrene and vinyltoluene contents of modified alkyds may be obtained from the ratios of absorbances at 14.2 μm and 12.4 μm respectively to that at 5.75 μm.

7. QUALITATIVE ANALYSIS OF CARBOXYLIC ACIDS IN ALKYD RESINS BY GAS CHROMATOGRAPHY

7.1 Scope

This method covers the qualitative determination of the carboxylic acids in alkyd resins, but may be also used for analysing polyesters.

7.2 Principle of the method

The acids in the resin are converted directly to the methyl esters with lithium methoxide in methanol.

The esters so formed are extracted with methylene chloride and submitted to gas chromatography on a polar and on a non-polar column.

The method has been worked out for a series of carboxylic acids, and the retention times relative to triacetin are given in *Table 1*. These retention times have to be considered as a guide to a satisfactory analysis, since variations with respect to apparatus, substrates, stationary phases, etc. may lead to deviations.

7.3 Reagents and auxiliaries

Methanol, absolute
Lithium
Sulphuric acid, 3M
Methylene chloride, pure
Saturated sodium chloride solution
Toluene, pure
Chloroform, pure
Magnesium sulphate, free of water
Triacetin.

7.4 Apparatus

Any linear programmed temperature chromatograph should be suitable, if adaptable to the operating conditions described below (*Note 1*).

Chromatography on a polar column

1. Column:	stationary phase	diethylene glycol succinate, Carbowax 20M
	solid support	Chromosorb W (sil.)
	length	2 m
	diam. (internal)	4.6 mm

2. Injection port temperature	320 °C
3. Column temperature	125–220 °C (rising 4 °C/min)
4. Carrier gas	He (flow rate 60 ml/min) (*Note 2*)

Chromatography on a non-polar column

1. Column: stationary phase	silicone grease DC II
solid support	Chromosorb W (sil.)
length	2 m
diam. (internal)	4.6 mm
2. Injection port temperature	320 °C
3. Column temperature	75–250 °C (rising 4 °C/min)
4. Carrier gas	He (flow rate 60 ml/min) (*Note 2*)

7.5 Column preparation

Polar column

Dissolve the diethylene glycol succinate (*Note 3*) in toluene and add the solution to the Chromosorb W (*Note 3*) in a porcelain dish in such a way that the weight ratio, stationary phase: solid support, is 10:90.

The solid support particles must be under the surface of the solution.

Remove the solvent on a water bath or with a stream of warm air while stirring the mixture gently with a spatula. After removing the solvent, heat in an oven for one night at 105°C.

Prepare in the same way as above a stationary phase of Carbowax 20M (*Note 3*) on Chromosorb W. Use chloroform instead of toluene as a solvent.

About 7.5–8 g of stationary phase and solid support is needed to fill a column of 2 m length and 4.6 mm (internal) diameter.

Pack the column subsequently in the following way:

Bring a piece of glass-wool into a 'U' shaped stainless steel column of the prescribed dimensions, dividing it approximately into two equal parts. One part is filled through a funnel with the polyester-containing phase, by gravity. The sides of the column are vibrated to assist the flow of the packing material. The other part is filled in the same way with the carbowax-containing phase.

Mount the column so that sample passes first through the polyester section.

Non-polar column

The stationary phase of the non-polar column is made in the same way as the polar column.

In this case the weight ratio, silicone grease:Chromosorb W (*Note 3*) is as before, 10:90.

Use chloroform as a solvent.

Packing of the column must be carried out by plugging one end of the column with a piece of glass-wool or a stop-cork and filling and vibrating as described before.

Note 1

If the apparatus is equipped with a hot wire type of detector it may be necessary sometimes, when only very small amounts of acids are present, to use a higher liquid phase:solid support ratio, e.g. 20:80. This is due to the lower sensitivity of this type of detector compared with flame ionization.

This may lead to deviations from the retention times given in *Table 1*.

Note 2

The use of helium as an elution gas is not necessary but the use of other gases may lead to different retention times (*Table 1*).

Note 3

Diethylene glycol succinate, Carbowax 20M (=polyethyleneglycol, m.wt. 20000) and silicone grease DC 11, are all commercially available. Chromosorb W (60–80 mesh; sil.) is a diatomaceous earth, specially treated and silanized. It is also commercially available.

7.6 Procedure

7.6.1 Sample preparation

In a round-bottomed flask weigh 0.3 g of alkyd resin, free of solvent, and add 15 ml of 0.5M lithium methoxide in methanol (*Note 4*). Dissolve the resin by heating on a water bath, and reflux for a few minutes. Then add 5 ml of 3M H_2SO_4, and transfer the contents of the flask to a separating funnel; dilute with water to 50 ml, add 35 ml of methylene chloride and shake. After separation of the methylene chloride layer, repeat the extraction with a further 35 ml of methylene chloride and combine the extracts. Wash this solution three times with 15 ml of saturated sodium chloride solution, dry over magnesium sulphate and distil off the methylene chloride in excess.

7.6.2 Chromatography

The recovered methyl esters are submitted directly to gas chromatography on polyester-carbowax as well as on silicone grease, following the operating conditions described in 7.1.

A drop of triacetin is added as internal standard.

A chromatogram without triacetin has also to be obtained, under the same conditions.

The amount of sample to be brought on the columns depends on the relative amounts of the acids in the sample and its concentration.

Note 4

The lithium methoxide is prepared by adding small pieces of metallic lithium to absolute methanol, which is cooled in an ice bath, until a 0.5M solution is obtained.

7.6.3 Identification

Identification is carried out with reference to the relative retention times listed in *Table 1*.

Table 1. Relative retention times for methylesters of carboxylic acids

Methyl ester of acid	Polyester carbowax column (triacetin = 1; ret. time = 11 min.)	Silicone grease column (triacetin = 1; ret. time = 16 min.)
succinic	0.26	0.38
benzoic	0.27	0.50
maleic	0.36	—
p-methyl benzoic	0.42	0.75
lauric	0.50	1.34
adipic	0.54	0.82
p-t-butyl benzoic	0.67	1·18
hexahydrophthalic	0.73	1.07
tetrahydrophthalic	0.89	1.08
p-hydroxybenzoic	0.97	1.05
azelaic	1·00	1.36
*endo*methylene tetrahydrophthalic	1.08	1.19
palmitic	1.15	2.04
sebacic	1.21	1.52
terephthalic	1.22	1.30
isophthalic	1.31	1.33
o-phthalic	1.31	1.20
stearic	1.53	2.34
oleic	1.53	2.30
linoleic	1.58	2.30
citric	1.65	1.22
linolenic	1.70	2.30
trimellitic	2.37	1.83

As it is not possible to standardize the method completely with respect to all possible variables, these retention values have to be considered as a guide. The real values must be determined by each operator under his conditions.

Precision and accuracy

The method described has been investigated in collaborative work by five laboratories. The constituents of two alkyds were determined correctly in most cases. Quantities of fatty acids as low as 5 per cent could be detected.

8. IDENTIFICATION AND SEMI-QUANTITATIVE DETERMINATION OF POLYOLS IN ALKYD RESINS BY GAS CHROMATOGRAPHY

8.1 Scope

This method covers the qualitative and semi-quantitative determination of the following polyols in alkyd resins: ethylene glycol, glycerol, trimethylol ethane, trimethylol propane, pentaerythritol and dipentaerythritol.

In principle it can be used for other polyols and for analysing polyesters.

8.2 Principle of the method

The alkyd resins are subjected to aminolysis with β-phenylethylamine and the liberated polyols acetylated. The polyol acetates are separated by

gas chromatography and identified from the relative retention time with reference to the second of the peaks given by the reagent. The amount is determined with the help of an internal standard.

The relative retention times given in *Table 2* have to be considered as a guide to satisfactory analysis since variations with respect to apparatus, substrates, stationary phases, etc. may lead to deviations.

8.3 Reagents and auxiliaries

β-phenylethylamine, pure.

Acetic anhydride, pure (distilled before use).

Various polyols, gas chromatographically pure.

8.4 Apparatus

Any linear programmed temperature gas chromatograph should be suitable, if adaptable to the operating conditions described below (*Note 1*).

8.5.1 Analysis of glycerol, ethylene glycol, trimethylol ethane, trimethylol propane and pentaerythritol

1. Column:	stationary phase	Carbowax 20M
	solid support	Chromosorb W (60–80 mesh, sil.)
	length	2.40 m
	diam. (internal)	4.6 mm
2. Injection port temperature		320°C
3. Column temperature		70–225°C (rising 8°C/min)
4. Carrier gas		He (flow rate 65 ml/min) (*Note 2*)

8.5.2 Analysis of dipentaerythritol

1. Column:	stationary phase	silicone gum rubber SE 30
	solid support	Chromosorb W (60–80 mesh, sil.)
	length	1.20 m
	diam. (internal)	4.6 mm
2. Injection port temperature		330°C
3. Column temperature		150–290°C (raising 6°C/min)
4. Carrier gas		He (flow rate 65 ml/min) (*Note 2*)

8.6 Column preparation

8.6.1 Carbowax column

Dissolve the Carbowax 20M (*Note 3*) in chloroform and add the solution to the Chromosorb W (*Note 3*) in a porcelain dish in such a way, that the weight ratio, stationary phase:solid support, is 10:90.

The solid support particles must be under the surface of the solution.

Remove the solvent on a water bath or with a stream of warm air while stirring the mixture gently with a spatula. After evaporation of the solvent, heat in an oven for one night at 105°C.

About 9–9.5 g of stationary phase solid support is needed to fill a column of 2.40 m length and 4.6 mm (inside) diameter.

Packing of the column must be carried out by plugging one end of the column with a piece of glass-wool or a stop-cork and filling through a funnel by gravity.

The sides of the column are vibrated to assist the flow of the packing material.

8.6.2 Silicone gum rubber column

Prepare in the same way as described above, a silicone gum rubber SE 30 (*Note 3*)/chromosorb W column.

Use toluene instead of chloroform as a solvent.

Note 1

If the apparatus is equipped with a hot wire type of detector it may be necessary sometimes, when only very small amounts of polyols are present, to use a higher liquid phase:solid support ratio, e.g. 20:80. This is due to the lower sensitivity of this type of detector compared with flame ionization. This may lead to deviations from the retention times given in *Table 2*.

Note 2

The use of helium as an elution gas is not necessary. The use of other gases may lead to different retention times (*Table 2*).

Note 3

Silicone gum rubber GE SE–30 (methyl silicone gum rubber) and Carbowax 20M (polyethylene glycol, m.wt. 20000), are both commercially available. Chromosorb W (60–80 mesh; sil.) is a diatomaceous earth, specially treated and silanized. It is also commercially available.

8.7 Procedure

8.7.1 Sample preparation

Add to 0.5 to 1 g of the alkyd resin, free of solvent, about 0.1 g of an internal standard (*Note 4*) both weighed to the nearest milligramme. To the mixture add 4 ml of β-phenylethylamine and heat in a round-bottom flask with ground-glass joint for 2 hours (*Note 5*) under reflux.

Add to the cooled mixture 25 ml of acetic anhydride, and heat for 2.5 hours under reflux.

After cooling, analyse the mixture of polyol acetates as such by gas chromatography.

8.7.2 Chromatography

The polyol acetates are submitted to gas chromatography following the operating conditions described in *8.5.1* (in the case of dipenta, *8.5.2*).

The amount of sample to be brought on the columns depends on the relative amounts of the polyols present in the sample and its concentration.

Note 4

As an internal standard a polyol not present in the alkyd must be used. Therefore in the first place sample preparation has to be carried out without internal standard in order to identify the polyols in the alkyd. In the case of dipentaerythritol, pentaerythritol must be used as internal standard. Because in most cases both are present, this can be done by determining

pentaerythritol on the carbowax column and using the value found to calculate the dipentaerythritol from the result on silicone gum rubber.

Note 5

In the case of dipentaerythritol this is 4 hours.

8.7.3 Identification

Identification is carried out with reference to the relative retention times listed in *Table 2* (*Note 4*).

Table 2a. Relative retention times of polyol acetates on a column of carbowax 20M

(second reagent peak = 1.00 (*Note 6*); retention time = 22 min)	
1,2 propanediol	0.46
ethylene glycol	0.48
neopentyl glycol	0.52
diethylene glycol	0.69
glycerol	0.73
trimethylol ethane	0.81
trimethylol propane	0.85
triethylene glycol	0.91
1st reagent peak	0.96
2nd reagent peak	1.00
pentaerythritol	1.09

Table 2b. Relative retention time of dipentaerythritol acetate on a SE 30 column

(penta = 1.00; retention time = 9 min)	
pentaerythritol	1.00
dipentaerythritol	2.50

As it is not possible to standardize the method completely with respect to all possible variables, these retention values have to be considered as a guide. The real values have to be determined by each operator under his own conditions.

Note 6

If identification required cf. De La Court, *Farbe und Lack*, **15**, 218 (1969).

8.7.4 Calculation

The weight percentage of polyol in the non-volatile resin is calculated from the formula:

$$\text{Per cent polyol} = f_x \times \frac{O_x}{O_1} \times \frac{g_1}{g_m} \times 100$$

f_x = conversion factor for the polyol in relation to the internal standard
O_x = area under the chromatographic peak of the determined polyol

O_1 = area under the chromatographic peak of the internal standard
g_1 = weight of the internal standard
g_m = weight of the non-volatile alkyd resin.

Precision and accuracy

The method described has been investigated in collaborative work by five laboratories.

The constituents of two alkyds were identified correctly in most cases.

Most laboratories found quantitative values lying within 10–15 per cent of the amount of polyol actually present.

The method is therefore considered as semi-quantitative.