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Part I

General Methods of Analysis of Drying Oils[1]

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TESTS are generally applied to drying oils to control quality and processes and to determine composition. These tests may be classified simply in the groups shown in Table I. Those test methods in italics are commonly used for quality control by buyer and seller. For process control saponification value, specific gravity, foots test, and heat break are dispensable. In the characterization of an oil any or all of the test methods may be necessary, but instrumental methods are valuable adjuncts and in certain cases may provide an unequivocal identity.

TABLE I

Analysis of Drying Oils

- CHEMICAL METHODS
  - *Iodine value*
  - *Hydroxyl value*
  - *Saponification value*
  - *Acid value*
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  - *Peroxide value*
  - *Unsaponifiable matter*
- PHYSICAL METHODS
  - *Viscosity*
  - *Color*
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- SPECIAL METHODS FOR DRYING OILS
  - *Foots test*
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  - *Gel time and heat-bodying rate*
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- INSTRUMENTAL METHODS
  - Ultraviolet spectrophotometry
  - Infrared Spectrophotometry
  - Gas chromatography

It would be impractical in this paper to describe all the above tests and their significance. Only a superficial discussion will be possible for most of them. It must be emphasized that, except for minor components and modifications, drying oils are esters of fatty acid mixtures. The properties of the drying oil are therefore a reflection of the fatty acid composition. In the past it was customary to run a multiplicity of tests or so-called analytical constants to gain information concerning this composition. With the introduction of highly sensitive infrared and ultraviolet spectrophotometers and gas chromatographs, such information becomes readily available, even on a routine or control basis, and many of the usual tests become superfluous.

Chemical Methods

Iodine Value. An iodine value does not adequately describe a drying oil but can serve as an excellent sorting test when used in conjunction with other tests. Oils may be simply classified by iodine value in accordance with the following scale (18).

Drying oils	160 and up
Semi-drying oils	120 to 160
Nondrying oils	below 120

The iodine value, which expresses the degree of unsaturation, is defined as the percentage of iodine absorbed by the sample, whether or not the halogen used is actually iodine. Iodine value determinations are empirical and require exacting technique. The Wijs method, favored in the United States and official within the American Oil Chemists' Society, utilizes iodine monochloride in acetic acid as the halogenating agent. The reagent is considered to be stable for at least 30 days and, when prepared with the proper

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[1] ADM Technical Talk No. 174.

TABLE II

Iodine Value Methods Applicable to Drying Oils

Method	Catalyst	Reaction time	Oils	Reference
Wijs	None	1 hour	Natural and synthetic	2, 4, 6, 30
Modified Wijs	Mercuric acetate	3–5 min.	Nonconjugated	14
Woburn	None	1 hour	Oiticica, tung and dehydrated castor oil	28
Rosenmund-Kuhnhenn	None	5 min.	Nonconjugated	23
Modified Rosenmund-Kuhnhenn	Mercuric acetate	1 min.	Nonconjugated	7
	Mercuric acetate	30–120 min.	Conjugated	17

ratio of iodine to chlorine, may be kept for more than a year (21). For reproducibility the reagent excess must be carefully controlled; this may be accomplished by varying the sample size. A reagent excess of 125 ± 25% will give uniform results with nonconjugated oils, but conjugated oils, such as tung, require strict control of reagent excess at 125 ± 10%. Other variables which must be controlled are the temperature of the reaction, 25° ± 5°C. for nonconjugated and 25° ± 1°C. for conjugated oils, and the time allowed for the halogen uptake, one hour (2).

When the iodine value of a conjugated oil is determined, the result is not a measure of the total unsaturation but is an empirical value which should be used only comparatively. To compensate for the low values, iodine value specifications have been set lower than the theoretical values based on hydrogen uptake. This undesirable situation has been deplored by many.

Several investigators have studied the Wijs method as applied to tung and dehydrated castor oil and have concluded that a large excess of reagent be used to obtain near theoretical values. A modified Rosenmund-Kuhnhenn method (23) also shows some merit for conjugate unsaturation and avoids the trouble caused by light.

Modification of the Wijs method through the addition of mercuric acetate will permit the reaction time to be shortened to three minutes (14). This might be of value for the study of processes which may be controlled through changes in unsaturation. When mercuric acetate is added to the Rosenmund-Kuhnhenn pyridine sulfate dibromide reagent, the reaction time is also shortened and consistent results may be obtained with conjugated oils, such as tung (7, 17).

In Table II are summarized iodine value methods which can be applied to drying oils.

Hydroxyl Value. The drying oils subcommittee of the A.O.C.S. (3) presently defines the hydroxyl value as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of sample. The acetyl value expresses the results in terms of the acetylated sample but has been almost completely superseded by the hydroxyl value. The two may be interconverted if desired by the following calculations:

$$A = \frac{H}{1.000 + .00075H}$$

$$H = \frac{A}{1.000 - .00075A}$$

A = acetyl value H = hydroxyl value

The procedure, recently approved by the A.O.C.S., employs acetic anhydride in pyridine as the acetylating agent, according to the equation:

$$\mathrm{ROH} + \mathrm{Ac_2O} \xrightarrow{\text{pyridine}} \mathrm{ROAc} + \mathrm{HOAc}$$

The excess reagent, remaining after acetylation, is hydrolyzed to acetic acid, which is titrated with standard alkali. Butyl alcohol is added before the titration to form a homogeneous solution.

In unmodified oils the hydroxyl value measures the small amount of hydroxy acids along with mono- and diglycerides formed in processing. Castor oil, predominately a glyceride of ricinoleic acid, has a relatively large hydroxyl value. In drying oil technology the hydroxyl method is useful in following the course of alcoholysis reactions, in determining the reactivity of polyhydric alcohols, and in the study of autoxidation.

Saponification and Acid Values. The saponification value is a measure of the alkali-reactive groups in oils and is useful in predicting the type of glycerides in a sample. Glycerides containing short-chain acids have higher saponification values than those with longer-chain acids. Blown oils, oils modified with maleic anhydride, and oils containing rosin acids show higher saponification values than natural oils. Thus the saponification value, along with the iodine determination, may be useful as a screening test, both in quality control and in characterization.

The saponification value is defined as the number of milligrams of potassium hydroxide that will react with one gram of sample (2). It is determined by refluxing the sample with an excess of alcoholic potassium hydroxide for one hour and titrating the excess base with standard acid. The saponification equivalent may be calculated from the saponification value and is the number of grams of oil reacting with 1,000 ml. of a *N* alkali solution. Expressed in this way, it is a measure of the equivalent weight of the ester groups.

$$\text{Saponification equivalent} = \frac{56108}{\text{saponification value}}$$

The ester value of the oil may be obtained by subtracting the alkali used for neutralizing the free acids from that required for the saponification.

Natural drying oils are no particular problem, but occasionally a modified drying oil is encountered that resists normal saponification treatment. In this

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case other saponification mixtures such as n-butyl alcohol and potassium hydroxide may be used (24) to obtain near-theoretical values. The solvent system ethanol-pyridine also yields satisfactory results for most modified drying oils, including oils copolymerized with styrene and dicyclopentadiene.

The acid value determination is perhaps the most widely used drying oils test. Much like the saponification value, it is the number of milligrams of potassium hydroxide required to neutralize the acids in one gram of sample. It is determined by dissolving the oil in a neutral solvent and titrating with standard alkali to a phenolphthalein endpoint. The A.O.C.S. procedure Ka 2-58 specifies a mixture of isopropyl alcohol and toluene and a titrant of sodium hydroxide in methanol (2). The acid value is used to indicate the quality of raw oils, as a control measure in the production of blown, bodied, and modified oils, and in the control of esterification reactions.

The acid value is a measure of average chain-length in commercial fatty acids and, as such, is used in conjunction in manufacture of alkyd resins, soaps, and other fatty acid derivatives. In research, the neutralization equivalent is used and is calculated from the acid value in a manner analogous to that used for the saponification equivalent. The neutralization equivalent more nearly characterizes the fatty acid in terms of its molecular weight.

Peroxide Value. The peroxide value is a measure of active oxygen in an oil and is defined as the number of equivalents of peroxide in 1,000 g. of oil. The Wheeler iodometric method (19, 29) with slight modification is the preferred method in the United States.

Although the method is highly empirical and requires strict control over the variables involved, it is of value as an indication of the quality of oil and, used with other tests, will detect incipient rancidity. In characterization the peroxide value is useful as a screening test for the peroxide content of bodied and blown oils is five to ten times greater than that of a normal oil.

The test is carried out in a one-phase system consisting of oil sample, chloroform, and acetic acid. The iodine liberated by the one-minute reaction between the peroxide and a saturated solution of potassium iodide is titrated with sodium thiosulfate in the conventional manner.

Unsaponifiable Matter. Any significant amount of material in a drying oil which does not saponify or is not water-soluble is likely to be either a contaminant or a modifying agent. Normally the unsaponifiable portion of an oil consists of sterols, alcohols, pigments, and hydrocarbons and will not exceed a few per cent. Thus the determination of unsaponifiable matter is important as a test for impurities and in the detection of modified oils.

Unsaponifiable matter may be isolated from a saponification mixture by repeated extraction with a hydrocarbon solvent and is commonly expressed as a percentage of the original sample weight.

Physical Methods

Viscosity. The viscosity of an oil is of doubtful importance as a sorting test because the viscosities of most oils vary slightly. However in the evaluation of products derived from the oils, such as varnishes, blown and bodied oils, and modified drying oils, viscosity is probably used more than any other test. The viscosity of the vehicle influences greatly the properties of the coating in which it is incorporated. Therefore the processor must use care in the control of viscosity in the manufacture of coating materials.

As a control test, viscosity measurements are of assistance in predicting the end-point in certain bodying and blowing reactions for, at a given reaction temperature, the log of the viscosity plotted *versus* time will give a straight line.

The falling ball and rising bubble methods are most popular among the many devices for measuring viscosity. The Gardner-Holt system, a direct comparison method, has a decided advantage in simplicity and speed but has a limitation in that high viscosities (Z and over) may not be adequately described by letter. The drying oils subcommittee is presently considering a number of systems which will avoid this situation. In the present method Ka 6-55 extremely high viscosities are expressed in time of bubble travel in seconds, or in stokes according to the formula:

$$\text{Viscosity (stokes)} = 0.73t - \frac{0.5}{t^2}$$

where t = time in seconds.

Color. The A.O.C.S. has sponsored three color methods, each designed for a specific class of oils. The F.A.C. method (3), used primarily with dark fats and oils, and the Wesson method both determine color comparison, the former with standards of definite composition and the latter with Lovibond glasses of known color characteristics. A photometric method (A.O.C.S. Tentative Method Ca 13c-50) is under study and will probably be modified before it becomes official.

The method currently in use (Ka 3-58) for drying oils is comparatively crude but has the advantage of speed and simplicity. Color is determined by comparison with 18 standards made with potassium chloroplatinate for the lighter tubes one through eight and ferric chloride and cobalt chloride for nine through eighteen. The chief disadvantage of the Gardner color system is that the reading must be based on a similarity in color density. If an oil has a green or red color, the comparison cannot be easily made and the reading is usually high. A minor drawback is the apparent instability of the chloroplatinate standards. It is hoped that a system can be devised that will have the advantage of the Gardner method without these shortcomings.

Specific Gravity. The specific gravity of drying oils varies from 0.9 to 0.99 and may exceed 1.00 for blown oils. Although not reliable for identification purposes, it is of significance to the designer of equipment for storage and processing and of importance in trading. The paint formulator is also concerned with specific gravity because the spread, when applied to a paint formulation, may have a bearing on its cost and performance.

The specific gravity of an oil is usually measured in a pycnometer. The Leach type (4) is recommended for oils with viscosities up to 500 stokes and wide-mouth specific-gravity bottles for more viscous oils. Entrapment of air bubbles should be avoided, and loss of oil should be prevented.

To convert from a specific gravity at one temperature to another temperature the following formula may be applied (10), in which 0.00065 is an average coefficient of expansion for oils.

$$d^{t_1}_{t_2} = \left[d^{t_3}_{t_4} - 0.00065\ (t_1 - t_3)\right] \frac{d^{\ t_4}_{(H_2O)}}{d^{\ t_2}_{(H_2O)}}$$

Special Methods for Drying Oils

Foots Test. The preceding tests have been the most important of the physical and chemical tests applied to drying oils. The foots test cannot be classified in either group and is the basis of much controversy. It is empirical and its purpose is obscure; nevertheless it is part of many specifications.

The term "foots" denotes material insoluble in a mixture of acetone, calcium chloride solution, and the oil under the specific conditions of the test (5). The test was designed specifically for linseed oil but is also applicable to other oils. Its purpose is probably to measure the amount of solids that will separate out of an oil on standing. Paradoxically there is no means of demonstrating that these solids and the foots are the same material.

In view of the poor reproducibility between laboratories running this test and the poor definition of the scope of the method it must be admitted that the method is not satisfactory, that it should be studied in committee and eliminated if it cannot be improved.

Break Test. The break test is similar to the foots test; both measure nonoil materials in crude oils. These materials, germs, pigments, and phospholipids, contribute to refining losses, adversely affect color and clarity of oils which are heated or blown, and perceptibly increase the drying time of the oil. They are largely removed during refining operations.

The modified Gardner break method (5) consists of heating to 290°C. 25 g. of oil to which have been added three drops of concentrated hydrochloric acid and of diluting the sample with carbon tetrachloride. The precipitated material is filtered with the aid of a weighed amount of diatomaceous silica, washed free of oil, and dried to constant weight at 105°C. Results are expressed as percentages. The A.S.T.M. method claims a precision of 0.02% of the sample taken, which is considerably better than the foots test.

Gel Time and Heat-Bodying Rate. Conjugated oils gel as a result of polymerization reactions. Both the gel time and heat-bodying rate are important to the varnish maker in order to attain high viscosity without gelation. The former is obtained by heating a 5-ml. sample at 282°C. in a test tube containing a stirring rod (5). The gel time, the time required for the oil to form a solid gel under the specified conditions of the test, is the point at which the oil becomes stiff enough so that the entire tube and its contents may be raised by the rod.

The heat-bodying rate (4) of drying oil is the rate gain of viscosity at a specified elevated temperature. A 700-g. sample of oil in an insulated beaker is heated to 307°C. and held at this temperature for eight hours or until the oil gels. Viscosity and color are determined at 0.5-hr. intervals. The viscosities are plotted against time on semilogarithmic paper with viscosities on the logarithmic scale. The average time required for the oil to double in viscosity is the heat-bodying rate. If an abrupt change in viscosity is noted and the curve shows two straight lines, this time is also reported. A new run is made at 293°C. if the oil gels within 2.5 hrs., and a third may be made at 274°C. if the oil still gels. The bodying rate approximately doubles with each increase of 12°–14°C. (27).

Drying Time. The measurement of the drying time should be one of the most significant tests applied to a drying oil. The process of measurement should be quite simple, but it is, in fact, one of the most poorly defined. In spite of the numerous mechanical devices (12) invented for the determination of drying time, one of the oldest instruments, a C. P. Finger, is still preferred by many operators.

The preparation of a uniform film is the first requirement in running the finger-touch method. This may be done by drawing down a film with a doctor blade. The sample is allowed to dry in a horizontal position at constant temperature and humidity, and the film is tested at intervals by lightly touching with the fingers. The "set to touch" time is that time at which the film does not transfer to the finger. When the finger may be drawn lightly across the surface without rubbing the film, the oil is considered to be at the "dust-free" stage, and when pressure of the thumb and finger causes no deformation or marking, the oil is said to be "dried hard."

Most of the instruments that have been designed for the determination of drying time, such as the Gardner Drying Time Master, the Sward Rocker, and the Zapon Tack Tester, are satisfactory, in that they are rapid and convenient and give reproducible data. Unfortunately they do not detect the stages in the drying of an oil defined above.

Acetone Number. A comparatively new test that is used both in control and in research is the acetone number. Acetone is soluble in unpolymerized oil but not in polymerized oil. The amount of acetone that will dissolve in an oil under the conditions of the test is a measure of the extent of polymerization. The method is simply a titration of the sample with anhydrous acetone to a permanent cloudiness, and the results are expressed in terms of a percentage of acetone dissolved (5).

According to Grummit *et al.* (13) the acetone number is a function of the type of oil and its viscosity, the amount of free acids, and the presence of modifying agents. In nonconjugated oils, such as linseed, the acetone tolerance varies inversely with viscosity up to a viscosity of about Z_6.

In order to obtain reproducible results the amount of water in the acetone must be strictly controlled as well as the temperature during the titration. Increased temperature increases the solubility of acetone in the oil and increasing amounts of water in the acetone cause the reverse to be true.

Nonvolatile. The A.O.C.S. does not yet recommend a method for the determination of nonvolatile matter in drying oils or vehicles. Those concerned with specifications and formulations therefore are left to their own devices, and, as a result, there is a great variety of procedures available for the determination of nonvolatile matter. The oven method is generally accepted. It consists of heating a sample in an oven at 105°C. for a specified length of time or to constant weight. Alternately a vacuum oven at 60°C. may be employed. Since most oven methods are not rapid enough for control work, a hot plate method has been under study by the drying oils subcommittee. This method calls for a 0.5-g. sample to be weighed into a 2.5-in. aluminum dish to which about one ml. of benzene is added. The sample is heated on a hot plate regulated at 150°C. for 15 min. The method is applicable to drying oils or vehicles mixed with volatile solvents, with the exception of highly bodied or blown oils. Lacquer oils may be run by the hot-plate method, using a temperature of 100°C. for 40 min.

Instrumental Methods

A discussion of instrumental methods used in the analysis of drying oils is properly reserved for another paper in this course. There are available to the analyst several instruments whose functions have become almost routine and which can help immeasurably in the characterization and evaluation of an oil. A brief discussion of the tentative ultraviolet and infrared methods approved by the Society is therefore in order.

It was stated previously that the properties of a drying oil are affected by the composition of its fatty acids. Gas liquid chromatography will readily provide the necessary information about this composition that can quickly solve the problems of identification and raw materials control. It is quite appropriate that some of the applications and implications of this relatively new analytical tool be considered here.

Ultraviolet Spectrophotometry. A.O.C.S. method Cd 7-48 (3) is based upon the absorption by conjugated fatty acids in the ultraviolet region. The characteristic wavelengths of the absorption are 233 mμ for dienes and 268 mμ for trienes. The tetraenes and more highly unsaturated acids display absorption at higher wavelengths.

In the presence of alkali at elevated temperatures, nonconjugated unsaturated fatty acids are partially isomerized to the corresponding conjugated acids. Through strict control of alkali concentration, time, and temperature, the course of the isomerization can be reproduced rather closely. If the isomerized sample, dissolved in alcohol, is examined spectrophotometrically at specified wavelengths, the resulting absorptivities may be compared with those obtained from standard samples. Thus the method permits the quantitative determination of di-, tri-, tetra-, and higher unsaturated components in drying oils. Saturated acids may be determined by difference, although with considerable error.

A.O.C.S. tentative method La 13-56 (2) is intended as a supplement to Cd 7-48 and includes in its scope dehydrated castor oil, dehydrated castor fatty acids, and their methyl or ethyl esters. No alkali isomerization is required in this method for the conjugated components being measured have been formed during processing of the oil or acids. The method determines the diene conjugation present, expressing this value as a percentage of conjugated dienoic acid and basing this value upon the absorbance of the sample at 233 mμ. It should be noted that the spectrophotometric determination of the various dienes in dehydrated castor oil is not entirely satisfactory. It has been demonstrated that the dehydration may lead to the formation of *cis-cis, cis-trans,* and probably *trans-trans* conjugated dienes (16, 20) and that the absorptivities of these isomers are not the same. An error is obviously introduced if one absorptivity is used to calculate the amount of conjugation in a mixture of all three.

Alpha- and *beta*-eleostearic acids may be determined in tung oil by a simple spectrophotometric procedure (15) that is based on the absorptivities at 271.5 and 269 mμ. The method is currently under study by the Spectroscopy Committee of the A.O.C.S.

Infrared Spectrophotometry. The identification of natural drying oils through their infrared spectra is not practical because of the similarity of certain spectra. Most oils, such as those of soybean and linseed, are virtually indistinguishable. The spectra of oils with conjugate unsaturation, tung, oiticica, and dehydrated castor, show minor differences in the region near 10 μ (8, 25) and castor oil, with an additional hydroxyl group, shows a strong absorption near 3 μ (25). With these exceptions the infrared spectra of unmodified oils offer little to the analyst.

Infrared spectroscopy is more valuable in the identification of modified oils containing dicyclopentadiene, vinyl toluene, styrene, and other materials which may be copolymerized or reacted with the drying oils. Often an oil can be identified through a comparison of its spectrum with that of a known specimen. The present published reference spectra are not abundant, but it is a relatively simple matter to obtain polymers of known composition, run their spectra, and build one's own file of spectra.

Reasonably quantitative methods have been suggested for determination of certain components in drying oils formulations. Acrylonitrile in polymers can be estimated from the intensity of absorption at 4.48 μ (1). Styrene in styrenated oils, alkyds and epoxy resin esters, is determined by a comparison of the peak at 14.3 μ with that at 5.75 μ for oils and alkyds and 12.1 μ for epoxy esters (11). The percentage of phthalic anhydride in an alkyd may be estimated from its infrared spectrum by calculating the ratio of the transmissions at 13.5 μ and 13.9 μ and referring this value to a standard curve prepared in a similar manner from alkyds of known composition. The accuracy of this latter method is about ± 4% of the amount present, and aromatic compounds which absorb in the same region interfere, but the method is rapid, requiring no more than 30 min., and convenient.

The applications of infrared spectroscopy mentioned are only a few of those being presently used in the analysis of coating materials. A further discussion of coating and vehicle analysis is obviously not possible here.

Infrared spectroscopy has been useful in the determination of isolated *trans* double bonds. A method, developed by Swern *et al.* (26) and based on the sharp absorption at 10.3 μ, has been recommended for adoption by a committee of the Society. It is more accurate, rapid, and specific than the older lead salt alcohol method of determining *trans*-components in mixtures.

Gas Chromatography. The technique of gas chromatography has presently reached a stage where it may be routinely applied to determine the fatty acid composition of drying oils. Since this fatty acid composition profoundly influences the properties of the oil and its chemical derivatives, a knowledge of this composition is of utmost importance. In the past the statement that no single test would characterize an oil was probably true, but in gas chromatography we have a method that almost completely satisfies this requirement.

The development of the linear polyesters of suc-

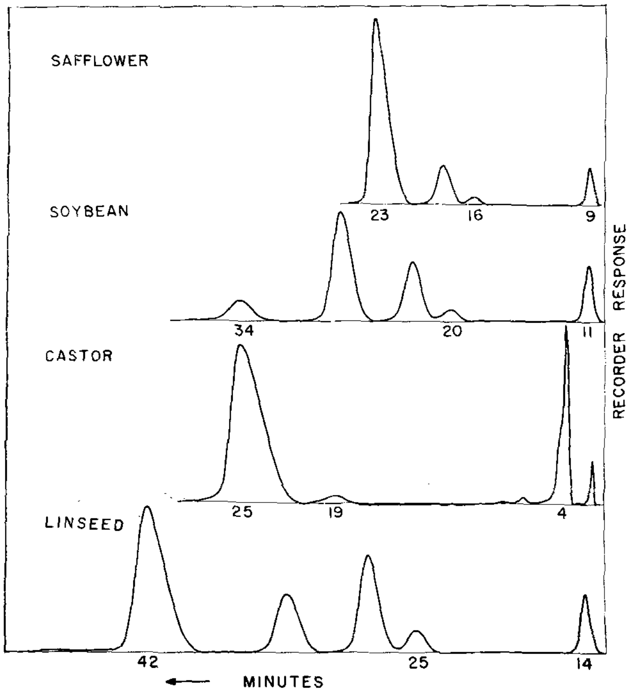

FIG. 1. Chromatogram of methyl esters of safflower, soy, linseed, and hydrogenated castor oil.

cinic anhydride and butanediol 1,4 as partitioning agents by Craig (9) has made possible the complete separation of the four C_{18} acids in mixtures of their methyl esters, using commercially available gas-chromatography equipment. These four acids represent the most difficultly separable components in most drying oils. The problem remaining is that of obtaining the necessary equipment and gaining enough technique to perform the separations.

Figure 1 shows the chromatograms of the methyl esters prepared from the respective oils. The samples were run on a Beckman GC-2 gas chromatograph, using columns of ¼-in. O.D. stainless steel with a Craig type of packing (25% by weight of the polyester on 60–80 mesh Chromosorb W), at temperatures from 225° to 240°C., and a sample size of .001 ml., with helium as the carrier gas.

The methyl ester prepared from hydrogenated castor oil was run on a 2.5-ft. column with a flow rate of 85 ml./min. and all others on a 6-ft. column at 40–45 ml./min. The composition of each sample is represented by the areas under the peaks, and these areas may be measured simply by integration. The first peak shown in the chromatograms of linseed, soybean, and safflower esters is that of methyl palmitate. A visual inspection is sufficient to identify the following four C_{18} acids, stearic, oleic, linoleic, and linolenic, if present. The first peak in the chromatogram of hydrogenated castor is methyl palmitate, the next larger peak is unresolved methyl stearate and oleate, and the last peak, the major component, is methyl hydroxy stearate. The differences in retention time for a given component in different esters is caused by variations in flow rates and column temperatures.

The fatty acid distributions of a group of oils analyzed by gas chromatography are shown in Table III. The values are in agreement with published values for these oils.

TABLE III

Fatty Acid Composition of Oils[a]

Oil	Iodine value	Sat. acids	Oleic	Linoleic	Linolenic
Perilla	203	8	14	14	64
Linseed	182	10	22	16	52
Hempseed	169	8	12	55	25
Soybean	133	15	25	51	9
Walnut	125	16	28	52	4
Sunflower	121	16	29	53	2
Safflower	144	11	13	76	0

[a] *Typical values from gas chromatography.*

In Table IV the Wijs iodine value of a group of oils is compared with the values calculated from gas chromatographic data. The agreement is good except for perilla oil, which contains a high percentage of linolenic acid, and a small amount of conjugated dienoic and trienoic acids. The utility of gas chromatography in the characterization of an oil is quite apparent from a consideration of these data. In most cases, measurement of peak areas is not necessary, and identification of the oil can be made by inspection. Even mixtures of drying oils may be detected by this means.

Although gas chromatography and its companion, infrared spectrophotometry, will not answer all the analytical questions of the drying oils technologist, they will furnish him with information, which, in the past, was not readily available. They will also tend to supplant and render irrelevant many "analytical constants" which might otherwise be requested with no regard for their scope or usefulness. The analyst can finally be in a position whereby he can provide specific answers without a multiplicity of tests.

TABLE IV

Comparison of Iodine Values of Oils

Oil	Calculated (GC)	Determined (Wijs)
Perilla	203	188
Linseed	182	184
Hempseed	169	170
Poppyseed	147	150
Walnut	125	115
Corn	125	125
Sunflower	121	113
Sugar cane	110	107
Peanut	101	98
Olive	86	86
Babassu	16	18

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Extraction Methods for Drying Oils

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THIS PAPER presents a general discussion of the methods of obtaining drying oils from oil-bearing materials from the view-point of processes, equipment, problems encountered, and cost considerations. As a general discussion, it is intended to serve as an introduction to the industry for young engineers and for people whose main interests lie in allied fields or nonengineering aspects of the industry. A number of combinations of the three basic methods, namely, solvent extraction, mechanical pressing, and hydraulic pressing, are discussed.

Centuries ago the Chinese carried out crushing by grinding under an edgestone and pressing in a wedge press; the wedges were driven in manually by hammering. The first step in modern processing came with the development of the hydraulic press in England in 1795. In the United States recorded history began about 1826 in Columbia, S. C., where a man named Waring operated hydraulic presses on flaxseed, sesame, and cottonseed. Linseed oil was his first product and the main reason for the existence of the mill.

The next significant step was the introduction of the continuous mechanical-pressing system. This reduced the investment required for larger capacities and oil recovered above a certain minimum. Solvent extraction followed in the United States on soybeans, which made economical very-large-capacity installations and more complete oil recovery. A natural consequence was the introduction of the combination of the two, the prepress system.

Extraction Methods

Oil is normally obtained from oil-bearing materials by one of three basic methods or combinations and variations of these. All these methods involve a physical separation of the oil from the remainder of the material rather than a chemical type of reaction in which one or all of the components loses its chemical identity. The three basic methods consist of a batch hydraulic-pressing in which the oil is squeezed out by exerting pressure on a mass of the oil-bearing material hydraulically; a continuous mechanical-pressing in which the material is conveyed (or extruded) through a gradually decreasing aperture and the oil is squeezed out by the resulting pressure; and solvent extraction in which the oil is taken into solution in a solvent, the solution is separated physically from the insoluble solids, and the oil is recovered from the solvent solution.

The most common systems in use on drying oils are continuous direct solvent-extraction; continuous mechanical pressing and continuous solvent-extraction (prepress process); continuous mechanical pressing (screw press or expeller process); batch hydraulic pressing plus batch solvent-extraction; batch hydraulic pressing; and batch solvent-extraction. These are approximately arranged in the order of commercial importance in the United States today. However the order is contingent upon the fact that indirectly soybean oil is a drying oil through modification. If not, continuous direct solvent-extraction is of minor importance. Several other combinations are possible and possibly even economically feasible (such as batch hydraulic pressing plus continuous solvent-extraction in the case of castor beans) but have not, as yet, found significant commercial usage.

Continuous Direct Solvent-Extraction. In this type of operation the raw material is first subjected to a cleaning operation to remove trash, stones, stems and leaves, and other foreign material which would impair operations, damage machinery, or affect product quality. This is usually followed by some means of holding a small supply of cleaned material and measuring and feeding it to the process. The next two steps involve size reduction, in order to reduce the dissolving time, and conditioning, in order to affect this size reduction without making an excessive amount of fine material. As in the case of soybean processing, these may be divided into two size-reduction operations with the conditioning intermediate. The prepared material is then extracted in a countercurrent manner (or some approach to it) with oil-free solvent. Fresh material is put in contact with solution (miscella), and the spent material leaves the extraction unit after being washed with oil-free solvent. The solution of oil in the solvent, after being completely separated from the residue solids, is then stripped of the solvent by boiling off the greater part by means of indirect steam heating, followed by open steam-sparging at elevated temperatures or under reduced pressure. Solvent is recovered from the solids by either direct or indirect steam-heating or a combination of both.

Figure 1 illustrates a continuous direct solvent-extraction operation through a simplified flowsheet for processing soybeans. In this case, as in the case of most of the oil-bearing materials, the solid residue is of importance also since it contains a valuable source of protein. Accordingly the extracted solid residue is carefully sized through screening and grinding to pro-