Testing of Drying Oils: Preliminary Evaluation For Use in Protective Coatings*

DON S. BOLLEY and E. C. GALLAGHER
National Lead Company Research Laboratories
Brooklyn, New York

THE industrial paint and varnish laboratories are faced today with the evaluation of a great number of new synthetic, modified, and refined drying oils of widely diversified types and characteristics. There are three general steps in the development of an oil from the time it is first revealed to the time it finds a commercial application. The first step is one of introduction. This may consist of running a few simple tests such as drying characteristics, rate of bodying, color, etc., or the oil may be introduced through reading an advertising claim, verbal discussion, or on theoretical grounds. In other words, sufficient evidence is presented to warrant further interest in the oil. The second step is the general evaluation. This should be sufficiently detailed, characterize the oil, discover its peculiarities, and indicate its probable value for various purposes. The third step is then practical application or actual use for certain definite purposes. Obviously, the first step does not limit itself to any systematic procedure while the third step also cannot be generalized since it is dependent upon the use of the oil. We are concerned with the second step, the general evaluation and characterization of the oil.

A general evaluation program for protective coatings to be practical must be carried out in a relatively short time. This eliminates the possibility of using long time exposure tests. The ideal scheme would be to obtain complete information in a short time. However, since at present we cannot fulfill one condition without neglecting the other, a compromise between the two must be effected. The following scheme outlines a systematic method for evaluating drying oils in approximately one month.

In a broad consideration of this evaluation scheme it should be kept in mind that many of the tests are empirical in nature and that many differences of opinion exist as to the best methods of conducting such tests. Finally, the value of the results and interpretation obtained from a number of the tests depend greatly upon the experience of the analyst or evaluator.

The best use can be made of the following evaluation scheme when an oil of known performance is included as a control. In order to obtain reliable comparisons it is important that oils of equal viscosities be considered. To simplify and make the scheme practical the following viscosities were chosen:

TABLE 1

Standard Viscosities

Gardner-Holdt	Poises
A	0.50
G	1.65
Q	4.35
Z2	36.20
Z5	98.50
Z8	590.00

The above viscosities are the most common viscosities used by the paint and varnish field. While there are a great many drying oils of viscosities other than these, it is believed all can be readily adjusted to one of these typical viscosities. The use of such a finite series allows a large number of the oils to be classified together for comparisons.

When the oil is evaluated, a series of constants are first determined for characterization. These constants follow. In this table and other subsequent tables of tests appearing in this paper, a reference is given wherever possible for each test listed. When no reference is given, a brief description of the method employed is given immediately following the table.

TABLE 2

Constants

1. Viscosity	ASTM D-154-43
2. Color	ASTM D-154-43
3. Appearance	
4. Odor	
5. Acid Value	ASTM D-555-41
6. Saponification Value	AOCS Cd 3-25
7. Acetyl Value	
8. Iodine Value	ASTM D-555-41
9. Diene Value	
10. % Unsaponifiable	AOCS Ca6a-40
11. % Ash	ASTM D-555-41
12. Refractive Index	ASTM D-555-41
13. Specific Gravity $\frac{15.5° C.}{15.5° C.}$	AOCS Cc10a-25

The appearance and odor of the material being examined are noted by observation. Appearance is expressed by noting clarity, sediment, etc. The odor is compared to the odor of raw, bodied, boiled, blown oil, etc. All the above constants with the possible exception of acetyl value and diene value may be carried out by well known methods which are fairly well standardized. Our preferred method for determining acetyl value (hydroxyl number) is one using pyridine and acetic anhydride as described by West, Hoagland, and Curtis (1).

The diene value is best determined using an ultraviolet absorption spectrophotometer. There are numerous references to this method in the literature. However, this instrument is rather costly and the determination requires considerable experience and time. A chemical diene value may be determined by measuring a quantitative reaction with maleic anhydride under specified conditions (2).

The next series of tests may be considered an examination of oil performance.

The bodying test consists in heating 700 grams of oil in quart metal beakers at adequate bodying temperatures. Samples of the oil are taken at regular specified intervals during the bodying test and these samples are examined for viscosity and color. From the results

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TABLE 3

Oil Performance

1. Bodying Test
    - Time to Q
    - Time to Z2
    - Time to Z5
    - Gel Time
    - Color at Q
    - Color at Z2
    - Color at Z5
2. Condition of Oil 18 hours at 40° F.
3. Compatibility (solution and film)
    - a) Low viscosity nitrocellulose
    - b) Low viscosity ethylcellulose
    - c) Cellulose acetate
    - d) VYHH vinyl solution
    - e) Urea formaldehyde
    - f) Modified alkyd
4. Drying Test (Drier Added 0.3% Pb; 0.03% Co)
    - Set to touch time
    - 24 Hr. dryness rating
    - 48 Hr. dryness rating
    - 96 Hr. dryness rating
    - 192 Hr. dryness rating
5. Sward Hardness
    - Taken at 24, 48, 96, and 192 hours
6. Cold Water Test
    - Time to whiten
    - Time to fail
7. Hot Water Test
    - Time to whiten
    - Condition after one hour
8. Alkali Test ....ASTM D-154-43
    - Time to whiten
    - Time to fail
9. Film Solubility (exposed and oxidized oil)
    - % soluble in water
    - % soluble in hexane
    - % soluble in acetone
    - % soluble in alcohol benzol
10. Reactivity (zinc oxide)....................ASTM D-479-40
    - Original viscosity—Ford Cup No. 4
    - % increase in 24 hr.
    - % increase in one week

obtained, the bodying rate and the color of the bodied oil can be determined.

Compatibility tests are carried out by mixing the oil with a solution of the resin and noting whether or not complete solution occurs, both as a solution and as a dried film. If any cloudiness occurs in either the film or solution, the oil is said to be incompatible with the specific resin.

In order to determine drying rate, standard drier is added to the oil in the amount of 0.3% lead and 0.03% cobalt. The oil and drier mixture is spread on a 4″ x 6″ glass panel and exposed to the air in a vertical position at 77° F. The set to touch time is taken and dryness ratings are read at 24, 48, 96, and 192 hours.

The system for applying dryness ratings is shown as follows:

TABLE 4

Oil Performance

Dryness Rating
1. As Applied
2. Heavy bodied oil
3. Surface dry in spots and remainder gel-like liquid
4. Set to touch
5. Surface dry thick film
6. Surface dry portions dried completely through
7. Surface dry, very tacky
8. Dry, very tacky, finger leaves no mark
9. Dry, some tack
10. Dry, no tack

The actual dryness ratings are reported by number as shown in Table 4.

The same panels that are used for drying tests may be used for running Sward hardness tests on the dried film. The Sward hardness tests are conducted with the conventional Sward Rocker previously adjusted to give one hundred swings on glass. These Sward hardness ratings are taken at 24, 48, 96, and 192 hours.

Three test tubes ¾″ x 6″ are coated with the oil and drier mix by dipping, and the coated test tubes are allowed to dry in a vertical position for 48 hours. After drying, one tube is immersed in cold distilled water, another in boiling distilled water, and a third in cold 3% caustic solution. In the cold water test the time to whiten and the time to fail are noted. The test tube is immersed in the boiling water for a period of one hour, and the time to whiten and the condition of the oil film after one hour immersion are noted. If the film has not failed after one-hour immersion, the tube is allowed to dry and recovery time noted. The tube immersed in alkali is observed for the time to whiten and the time to fail. By failure is meant removal of film from the tube.

A mixture of oil and washed sea sand containing 10% oil is exposed under a sunlamp at a temperature of 77° F. for a period of three weeks. At the end of this time portions of the oil-sand mix are extracted with water, hexane, acetone, and an azeotropic mixture of alcohol and benzol. The apparatus used for extracting the sand-oil mixture is the conventional ASTM Rubber Extraction Apparatus. The per cent extracted is determined after a three-hour extraction period and the acid value of the extracted material is also determined. The results obtained yield information on the extent and type of breakdown of the oil film during exposure.

The reactivity test is conducted according to the regular ASTM method using Green Seal Zinc Oxide. The results are reported as the original viscosity obtained using a Ford Cup No. 4, the per cent increase in 24 hours, and the per cent increase in viscosity in one week.

WE have now examined the oil for its regular constants and for its performance both in the undried and dried states. The next step is to evaluate the oil in paints. To accomplish this the oil is made up into two paints; one containing single pigment zinc sulfide (this might be considered a nonreactive pigment); the other is a mixed paint formula containing white lead, titanium dioxide, zinc oxide, and asbestine. It is a reactive pigment mixture. The two paints are made up with drier and mineral spirits in a standard manner using a conventional laboratory three roller mill.

The paints are applied on a white primed wood panel using a 2½-inch paint brush. The application characteristics of the paint are reported on appearance, brushing, leveling, and gloss. These are reported as good, fair, poor, or bad. Consistencies on the paints are determined at one and seven days aging using a regular Stormer viscosimeter. Primed metal panels are painted and are allowed to dry at 77° F. for four hours in a constant temperature room. The panels are then exposed under a S-1 sunlamp for a period of ten days. One half of each paint panel is masked with black paper. At the

TABLE 5

Single and Mixed Pigment Paints

1. Appearance
2. Brushing
3. Leveling
4. Gloss
5. Consistency 1 and 7 days................ASTM D-562-44
6. After yellowing
7. Dry to touch at 77° F.
8. Dry to touch at 40° F.
9. Dry to touch at 230° F.
10. Drying odor
11. Wrinkling
12. Hardness 1 and 7 days
13. Water permeability (3)
14. Flexibility ....ASTM D-522-41
15. Elongation of stripped film (4)
16. Tensile strength (4)
17. Taber abrasion
18. Shear hardness
19. Adhesion
20. Sward hardness
21. Gloss ....ASTM D-523-44T
22. Color

end of the ten-day period the black paper is removed and after yellowing characteristics reported as none, slight, considerable, or bad. Drying tests at different temperatures are conducted on metal panels coated with the paint to be examined. The drying tests at 77° F. are run in a constant temperature room; those at 40° F. are run in a conventional refrigerator, and those at 230° F. are run under a heat source such as an infra-red baking unit. The drying odor is noted by immersing a small ball of steel wool in the paint. The ball is allowed to air dry for five hours and placed in a covered, round, glass, eight-ounce jar. After one day, the cover of the jar is removed and the odor noted and reported as none, mild, faint, or strong. The hardness test is conducted using the standard fingernail procedure on the panel which was dried at 77° F. Results are reported as soft, firm, or hard.

Water permeability test is conducted according to the method outlined by the National Paint, Varnish, and Lacquer Association(3) using a Payne permeability cup. Flexibility determinations are conducted on a conical mandrel. The paints are applied to tin plates and after drying are removed with mercury and the stripped films tested for elongation and tensile strength using a Gardner tensile strength machine as outlined by the National Paint, Varnish, and Lacquer Association. Taber abrasion, shear hardness, and adhesion are conducted according to the standard method outlined for users of the Taber abraser. Gloss on the dried film is read using a Hunter Multipurpose Reflectometer. Readings are taken at an angle of 60°. Color is reported by noting discoloration.

IF the oil being examined is to be used or is recommended as a varnish oil, it must be evaluated in varnish formulas. To accomplish this three 35-gallon varnishes are made up, all having a 50% volatile content, and a finished viscosity of D to F. The three varnishes which are made up contain the following resins respectively:

4% Limed Rosin
Phenolic Resin (Bakelite BR 254)
Maleic Resin (Amberol 801)

A complete inspection of the varnishes is made by determining the following values:

TABLE 6

35 Gallon Varnishes

1. Cooking Time
2. Cooking Loss
3. Viscosity as Made............................ASTM D-154-43
4. Viscosity After 1 Month.................ASTM D-154-43
5. Condition After 1 Month
6. Color Before Drier Addition...........ASTM D-154-43
7. Color After Drier Addition............ASTM D-154-43
8. Acid Value ....ASTM D-555-41
9. Per Cent Solids.................................ASTM D-154-43
10. Drying Test
    - Set to touch
    - Dust-free
    - Dryness ratings at 8, 24, 48, 96, and 192 hours
11. Sward Hardness
    - 24, 48, 96, and 192 hours
12. Kauri Reduction...............................ASTM D-154-43
13. Cold Water Resistance
    - Time to whiten
    - Time to fail
14. Hot Water Resistance
    - Time to whiten
    - Condition after 1 hour
15. Alkali Resistance
    - Time to whiten
    - Time to fail

Cooking loss is determined by weighing the varnish ingredients before and after varnish formulation. Dryness ratings are taken using the procedure outlined for testing the drying rate of oils, as are the Sward hardness, cold water, hot water, and alkali resistance tests.

The correlation of all the results obtained according to the above described procedures should enable the paint or varnish manufacturer to determine whether or not the oil should be subjected to long time exposure tests or if this is not practical, accept it for use. It is needless to say that adequate controls must be included with standard oils so that comparisons can be drawn. In order to illustrate this evaluation procedure, comparison is drawn showing some differences obtained on a regular alkali refined linseed oil and a synthetic linseed fatty acid pentaerythritol ester.

TABLE 7

Comparison of a Bodied Alkali Refined and a Synthetic Oil

	Bodied Alkali Refined	Synthetic
Bodying Rate		
Gel time	252 min.	120 min.
Color of Bodied Oil		
At Z2	9	13
Drying Rate		
Set to touch time	3½ hr.	2½ hr.
Abrasion Resistance		
Taber abrasion	339	200
Tensile Strength	5	20
Compatibility		
Urea formaldehyde	Incompatible	Compatible
Toughness		
Kauri reduction (phenolic)	130	150
Alkali Resistance		
Phenolic	27 hr.	114 hr.
Maleic	40 min.	32 min.
Limed Rosin	25 min.	62 min.
Film Solubility		
Alcohol-benzol	48.6%	37.0%
Acetone	44.6%	33.9%
Water	10.4%	10.5%
Hexane	21.3%	17.8%

The comparison of results shown in Table 7 show that the synthetic oil is much faster in bodying rate, slightly poorer in color of bodied oil, faster drying, harder, stronger, and perhaps somewhat tougher than the bodied alkali refined oil. In addition, the synthetic oil shows remarkable alkali resistance in varnishes; moreover, the results obtained on film solubility would indicate that the synthetic oil had broken down or decomposed to a much lesser extent on exposure than the alkali refined oil. Table 7 shows significant differences between the two oils. In other respects, the oils can be considered similar. It can easily be seen that the synthetic oil has definite advantages over the natural oil and in this case would be seriously considered for general use.

The evaluation program outlined above is subject to considerable change and modification as our experience and knowledge of oils increase. In addition, it is hoped that it may be expanded to give information to fields other than the protective coating, such as printing inks, patent leather, core binders, linoleum, etc. The value of conducting such a study becomes more apparent after a large number of oils have been so tested and the information collected and examined. It would be extremely useful to the consumer if the industry could standardize on an evaluation program and have available information on the various oils in a standard and uniform manner. Perhaps, this would not be practical at present, but it is presented as an idea for discussion.

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Vapor Phase Dehydrochlorination of Chlorinated Fatty Substances

I. Investigation of Removal of Hydrogen Chloride from Dichlorinated Palmitic Acids*

G. R. VAN ATTA, D. F. HOUSTON, and W. C. DIETRICH

Western Regional Research Laboratory,[1] Albany, California

Introduction

WARTIME curtailment of imported soap and paint oils prompted this inquiry into possible methods for desaturating long-chain fatty acids. Considerable advance has been made in the past decade in commercial development of derivatives formed by operations on the carboxyl groups (1). Corresponding methods of modifying the comparatively inert alkyl portion of these acids have not been as satisfactorily developed. Among the agents that react with the alkyl chains, the halogens, and more particularly chlorine, appeared to provide the best means for obtaining suitable intermediate derivatives. Partial chlorination of a single saturated fatty acid, such as palmitic, yields a mixture of products of differing degrees of chlorination with chlorine atoms at various chain positions. Subsequent removal of chlorine as hydrogen chloride presents the possibility of forming unsaturated acids that might be commercially useful or could be made so by isomerization.

Reported treatments for removal or replacement of chlorine may be grouped in two classes: a) Hydrolytic processes tending to give differing proportions of hydroxylation and unsaturation in the products, and b) thermal or catalytic dehydrochlorination under acid conditions.

Hydrolytic processes have commonly been utilized at atmospheric or superatmospheric pressures (2, 3, 4, 5, 6) at times in the presence of organic solutions of ammonia (7) or of solutions of sulfides or polysulfides (8). Treatment of salts of chlorinated acids in steam at temperatures above their melting points for formation of soaps of unsaturated acids has been recently patented (9). Thermal dehydrochlorination of chlorinated oils, according to Gardner and Bielous (10, 11) resulted in oils of increased drying properties. Approximately one half of the chlorine was removed by heating chlorinated oils containing between 5 and 12% of chlorine to 220-250° C. at atmospheric pressure in the presence of coppered-zinc. This catalyst was believed to aid in the production of polymerized compounds. Meunier and Wierzchowski (12) commented on the partial loss of hydrogen chloride when chlorinated oils were heated above 100° C. Scheiber (13) added chlorine to unsaturated oils and subsequently desaturated the chlorinated materials by heating in the presence of metallic zinc. Enhanced drying properties were claimed for the products. Vanin and Chernoyarova (14) added hydrogen chloride to oleic and petroselinic acids and obtained isomeric monounsaturated acids as the result of heating the chlorinated materials with nickel carbonate at 190-210° C. for three hours. The passage of chlorinated acids or esters, together with an alcohol or ether, over a heated solid catalyst is reported by Andrussow and Stein (15) to yield unsaturated compounds and alkyl halides.

In many of these earlier investigations a considerable proportion of chlorine remained in the final product. Investigations in this laboratory have shown that hydrogen chloride is readily removed from vaporized chlorinated fatty acids on passage at reduced

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.