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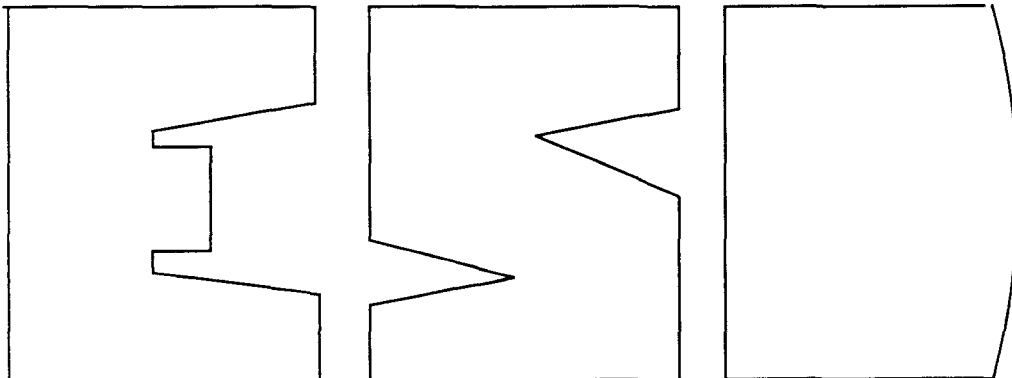
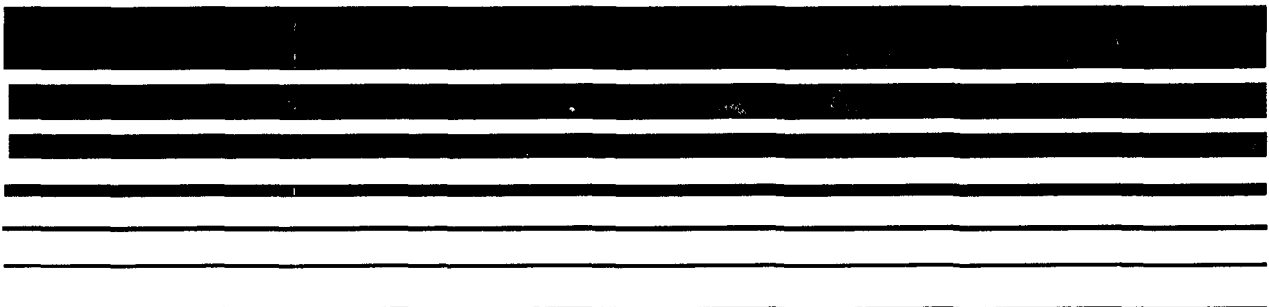
Office of Air Quality  
Planning and Standards  
Research Triangle Park NC 27711

EPA-450/3-91-011  
April 1991

Air



# The Impact of Declaring Soybean Oil Exempt from VOC Regulations on the Coatings Program



**The Impact of Declaring Soybean Oil  
Exempt from VOC regulations  
on the Coatings Program**

**Final Report**

EPA Contract No. 68-02-4378  
Work Assignment 138  
ESD Project No. 89/12A  
Radian Project No. 239-017-38

April 1991

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Publication No. EPA-450/3-91-011

## ACKNOWLEDGEMENTS

We acknowledge Candace Blackley and Joan Bursey of the Radian Corporation who carried out a great deal of the research and initial preparation of the report in fulfillment of assignments under EPA Contract 68-02-4378. Thanks are due to Ms. Rima Dishakjian of the Emission Measurement Branch, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency for conducting the Method 24 and 24A analyses. We appreciate the efforts of Mr. Dave Ailor of the National Oil Processor's Association for coordinating most of the oil samples, and Dr. Stoil Dirlikov for the vernonia oil sample and technical information. Further thanks go to Dr. Len O'Neil of the Paint Research Association for sending the papers and bulletins on the numerous studies undertaken by him in the 1940's and 50's.



## TABLE OF CONTENTS

	Page
1.0 INTRODUCTION .....	1
2.0 CONCLUSIONS .....	3
3.0 CHEMICAL & PHYSICAL PROPERTIES .....	5
3.1 FATTY ACID COMPOSITION .....	5
3.2 DRYING CLASSIFICATION .....	9
3.3 VOLATILITY/PHOTOCHEMICAL REACTIVITY .....	10
3.4 THERMAL STABILITY .....	12
3.5 INDIVIDUAL OILS .....	12
3.5.1 <u>Canola Oil</u> .....	12
3.5.2 <u>Castor Oil</u> .....	13
3.5.3 <u>Coconut Oil</u> .....	13
3.5.4 <u>Cottonseed Oil</u> .....	14
3.5.5 <u>Linseed Oil</u> .....	14
3.5.6 <u>Safflower Oil</u> .....	15
3.5.7 <u>Soybean Oil</u> .....	15
3.5.8 <u>Sunflower Oil</u> .....	18
3.5.9 <u>Tung Oil</u> .....	18
3.5.10 <u>Vernonia Oil</u> .....	19
4.0 PROCESSING AND REFINING VEGETABLE SEED OILS .....	21
5.0 DRYING/CURING PROCESSES .....	23
5.1 OXIDATION .....	23
5.2 CHEMICAL REACTIONS OF THE DRYING/CURING PROCESS .....	24
5.3 PRODUCTS OF COATING OXIDATION .....	25
6.0 VOC TEST PROCEDURES AND FINDINGS .....	27
6.1 TESTS CONDUCTED BY THE PAINT RESEARCH ASSOCIATION .....	28
6.2 APPLICATION OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUES .....	29
6.3 VOC TEST RESULTS .....	30
7.0 IMPACT OF TEST RESULTS ON TEST METHODS AND REGULATIONS .....	33
8.0 REFERENCES .....	35

## TABLE OF CONTENTS

	Page
1.0 INTRODUCTION .....	1
2.0 CONCLUSIONS .....	3
3.0 CHEMICAL & PHYSICAL PROPERTIES .....	5
3.1 FATTY ACID COMPOSITION .....	5
3.2 DRYING CLASSIFICATION .....	9
3.3 VOLATILITY/PHOTOCHEMICAL REACTIVITY .....	10
3.4 THERMAL STABILITY .....	12
3.5 INDIVIDUAL OILS .....	12
3.5.1 <u>Canola Oil</u> .....	12
3.5.2 <u>Castor Oil</u> .....	13
3.5.3 <u>Coconut Oil</u> .....	13
3.5.4 <u>Cottonseed Oil</u> .....	14
3.5.5 <u>Linseed Oil</u> .....	14
3.5.6 <u>Safflower Oil</u> .....	15
3.5.7 <u>Soybean Oil</u> .....	15
3.5.8 <u>Sunflower Oil</u> .....	18
3.5.9 <u>Tung Oil</u> .....	18
3.5.10 <u>Vernonia Oil</u> .....	19
4.0 PROCESSING AND REFINING VEGETABLE SEED OILS .....	20
5.0 DRYING/CURING PROCESSES .....	21
5.1 OXIDATION .....	21
5.2 CHEMICAL REACTIONS OF THE DRYING/CURING PROCESS .....	22
5.3 PRODUCTS OF COATING OXIDATION .....	23
6.0 VOC TEST PROCEDURES AND FINDINGS .....	24
6.1 TESTS CONDUCTED BY THE PAINT RESEARCH ASSOCIATION .....	25
6.2 APPLICATION OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUES .....	26
6.3 VOC TEST RESULTS .....	27
7.0 IMPACT OF TEST RESULTS ON TEST METHODS AND REGULATIONS .....	30
8.0 REFERENCES .....	32

## LIST OF TABLES

	Page
Table 3-1 CHARACTERISTICS OF VEGETABLE SEED OILS	8
Table 3-2 FATTY ACID CONTENT OF COMMON OILS	9
Table 3-3 COMPOSITION OF NORMAL FATTY ACIDS	10
Table 6-1 TEST RESULTS	29





## 1.0 INTRODUCTION

A food processing facility alleged that soybean oil used in frying its products should not be classified as a volatile organic compound (VOC) because its very low vapor pressure would preclude it becoming airborne, hence it could not contribute to photochemically produced ozone in the troposphere.

In addition to widespread use in the food industry, soybean and other vegetable oils are constituents in some inks, paints, and perhaps, other coatings. Thus the ramifications of any decision to declare it non-photochemically reactive on the longstanding regulatory program for coatings were important. This project was initiated to resolve the following questions:

Does soybean oil contribute VOC's to the atmosphere? In other words, is soybean oil an ozone precursor?

Is soybean oil unique among the vegetable oils? Are its physical characteristics significantly different from other vegetable seed oils in terms that would affect its potential to be a precursor to ozone formation?

What impact would declaring soybean oil exempt from VOC regulations have on current testing procedures and regulatory compliance programs for coatings?

This report presents the results of an investigation which addressed these questions. The information was obtained from a literature search, contacts in industry and academia, and limited experimental analyses. The literature search included the following computerized databases: Chemical Abstracts, Predicast Terminal System Predicasts Overview of Marketing and Technology (PTS PROMPT), Food Science and Technology Abstracts (FSTA), Agricola, CAB Abstracts, and Biosis Previews. Tables were prepared to compare various characteristics of ten vegetable seed oils (some of which are frequently found in coatings): canola, castor, coconut, cottonseed, linseed, safflower, soybean, sunflower, tung, and vernonia oils. The common uses and availability of each oil were identified, and the oil bean refining and drying/curing processes were examined. Studies of the VOC associated with vegetable

oil oxidation were reviewed, and test results applying EPA's reference methods 24 (RM-24) and 24A (RM-24A) for measuring VOC's in coatings to various vegetable oils were analyzed.

Section 2.0 contains the summary and conclusions. Section 3.0 discusses chemical and physical properties and general characteristics of the oils. Refining processes are described in Section 4.0 and drying/curing processes in Section 5.0. Section 6.0 discusses VOC test procedures and findings. Regulatory impacts are included in Section 7.0. Section 8.0 contains the references and Section 9.0 the Appendices.

## 2.0 CONCLUSIONS

- 1) A decision to exempt soybean oils from VOC regulation will have no effect on the longstanding VOC reduction program associated with coatings.
- 2) Soybean oil and other vegetable seed oils have no measurable vapor pressure at room temperature and atmospheric pressure.
- 3) None of the vegetable seed oils analyzed with EPA Method 24 (RM-24) or EPA Method 24A (RM-24A) contained a measurable amount of VOC.
- 4) Some samples analyzed by RM-24 or RM-24A actually gained weight (presence of VOC would normally cause a weight loss.)
- 5) Enforcement of air pollution regulations using RM-24 and RM-24A would not falsely jeopardize a source using coatings with a vegetable oil constituent.
- 6) Soybean oil, like the other vegetable seed oils listed in Table 3-1, is a complex fatty acid triglyceride.
- 7) The literature provides no obvious evidence that soybean oil can be distinguished from other vegetable seed oils in any significant way from the standpoint of volatility or photochemical reactivity.
- 8) Vegetable oils vary somewhat in physical properties and from batch to batch because of weather, soil and species.
- 9) All vegetable seed oils autoxidize when exposed to air. The resulting oxidation reaction cleaves the molecule with formation of some amount of many VOC's, chiefly hydrocarbons and aldehydes.
- 10) Oxidation is the mechanism by which coatings containing vegetable seed oils dry or cure.
- 11) Soybean oil will not boil at atmospheric pressure. Progressively increasing application of heat ultimately chars the oil, thermally cracking the fatty acid triglycerides to release hydrocarbons and aldehydes, precursors of ozone.

- 12) Soybean oil can contribute to ozone formation\*, as a precursor of VOC, although the contribution has not been quantified.
- 13) Since autoxidation of oils is a surface phenomenon, any process which maximizes the surface area of the oil will accelerate the autoxidation process. Thus, processes which employ oil as a mist or spray accelerate the oxidation of the oil and increase the release of ozone precursors.
- 14) This program, with a primary focus on the use of oils in the coatings arena, has posed new questions regarding volatile organic compounds which may be released in the food industry from processes involving cooking of foods in heated oils and spraying of oils. Appendix iv provides a list of references on this topic obtained from a computerized literature search.

Note that any attempt to sample a hot stack above a soybean oil cooking process poses challenges. A typical VOC sampling arrangement distinguishes between particulate and gaseous phases. One would normally conclude that the ozone precursors are present in the gaseous phase. Clearly, that would not be the case here. Inasmuch as the oxidation of soybean oils is not a rapid process, little of the ozone precursors would be formed in the stack. As a result, the total ozone formation potential of the exhaust gas includes the VOC in the gas phase and some unknown portion of the aerosol in the particulate phase.

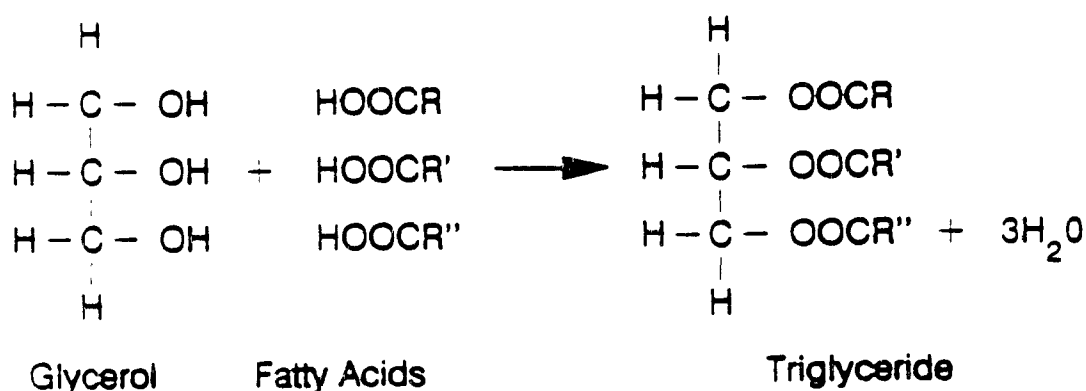
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\*Although not a product of this study, clearly the addition of moisture-laden foodstuffs such as potatoes, apples, and other materials to hot cooking oils causes splattering of the oil. The airborne particles have dramatically increased surface to mass ratios which would accelerate the oxidation reaction. Further, many of the foodstuffs are complex carbohydrates which, during cooking, can and do thermally crack to form lower molecular weight more volatile organic compounds which become airborne and available to participate in photochemical chemistry. Odorous compounds during the cooking operation are evidence of these volatile organic materials.

### 3.0 CHEMICAL & PHYSICAL PROPERTIES

#### 3.1 FATTY ACID COMPOSITION

Vegetable seed oils are water-insoluble substances of vegetable origin. Chemically they are triglycerides, i.e., compounds made up of glycerol-esters of long chain fatty acids.<sup>1</sup>



Since more than one kind of fatty acid is usually present, most vegetable oils are mixed triglycerides. The type of fatty acid found in the oil is the most important factor influencing the properties of the vegetable oils.<sup>2</sup> Most vegetable oils are composed of fatty acids with 18 carbon chains with varying degrees of unsaturation (containing double bonds). Examples of common saturated fatty acids are caprylic (C8), capric (C10), lauric (C12), myristic (C14), palmitic (C16), and stearic (C18).<sup>3</sup> Common unsaturated fatty acids include oleic (C18), linoleic (C18), linolenic (C18), alpha-eleostearic (C18), beta-eleostearic (C18), and ricinoleic (C18).<sup>4</sup> Tables 3-1 and 3-2 show the predominant fatty acids found in the ten selected oils. Table 3-3 shows the composition of these fatty acids. The type and percentage of fatty acids vary from oil to oil. For example,

Table 3-1 Characteristics of Vegetable Seed Oils

TYPE OF OIL	COST (\$/LB)	SALES VOLUME FOOD/NON FOOD (LB/YR)	DRYING CLASSIFICATION	OIL CONTENT OF SEED (%)	PREDOMINANT FATTY ACID COMPOSITION (%)	ACID VALUE	IODINE VALUE	SAPONIFICATION VALUE	SMOKE POINT (Celsius)
Canola	-	500 MMlb <sup>b</sup>	-	42 <sup>h</sup>	58 <sup>h</sup> (oleic)	-	112 <sup>h</sup>	190 <sup>h</sup>	232 <sup>c</sup>
Castor	0 405 <sup>a</sup>	-	Non-drying <sup>e</sup>	45 <sup>a</sup>	87 <sup>a</sup> (ricinoleic)	5 <sup>a</sup>	85 <sup>c</sup>	180 <sup>a</sup>	-
Coconut	0 27 <sup>1</sup>	-	Non-drying <sup>e</sup>	65 <sup>a</sup>	44 <sup>a</sup> (lauric)	2 <sup>a</sup>	10 <sup>c</sup>	250 <sup>a</sup>	-
Cottonseed	-	917 MMlb <sup>1</sup>	Non-drying <sup>e</sup>	20 <sup>g</sup>	40 <sup>a</sup> (linoleic)	1 <sup>a</sup>	106 <sup>c</sup>	190 <sup>a</sup>	245 <sup>d</sup>
Linseed	0 36 <sup>1</sup>	-	Drying <sup>e</sup>	35 <sup>a</sup>	52 <sup>a</sup> (linolenic)	4 <sup>a</sup>	174 <sup>c</sup>	190 <sup>a</sup>	-
Safflower	-	-	Semi drying <sup>e</sup>	30 <sup>a</sup>	75 <sup>a</sup> (linoleic)	4 <sup>a</sup>	145 <sup>c</sup>	190 <sup>a</sup>	-
Soybean	0 25 <sup>1</sup>	12 Bil lb <sup>b</sup>	Semi drying <sup>e</sup>	18 <sup>a</sup>	51 <sup>a</sup> (linoleic)	3 <sup>a</sup>	130 <sup>c</sup>	190 <sup>a</sup>	224 <sup>c</sup>
Sunflower	-	-	Semi drying <sup>e</sup>	29 <sup>a</sup>	52 <sup>a</sup> (linoleic)	4 <sup>a</sup>	125 <sup>c</sup>	190 <sup>a</sup>	230 <sup>c</sup>
Tung	0 53 <sup>1</sup>	-	Drying <sup>e</sup>	50 <sup>a</sup>	80 <sup>a</sup> (eleostearic)	8 <sup>a</sup>	168 <sup>c</sup>	190 <sup>a</sup>	-
Vernonia	0 60 <sup>1</sup>	-	-	42 <sup>1</sup>	80 <sup>1</sup> (vernolic)	1 <sup>1</sup>	90 <sup>1</sup>	-	-

<sup>a</sup> American Paint and Coatings Journal, November 5, 1990

<sup>b</sup> CPI Purchasing, October, 1990

<sup>c</sup> Chemical & Process Technology Encyclopedia, 1974

<sup>d</sup> Bailey's Industrial Oil and Fat Products, Vol I, Fourth Edition, 1979

<sup>e</sup> Federation Series on Coatings Technology, August, 1974

<sup>1</sup> Modern Paints and Coatings, August, 1990

<sup>g</sup> Vegetable Fats and Oils, ACS Series, 1954

<sup>h</sup> Canola Council of Canada, Product Information, 1990

<sup>1</sup> Journal of Commerce, July 26, 1990

<sup>1</sup> Telecon with Stoll Dirlikov, March 8, 1991

" " not found in search/literature

Table 3-2 Fatty Acid Content of Common Oils<sup>a,b</sup>

	Boiling Point (°C) <sup>c</sup>	Tung	Canola <sup>e</sup>	Castor	Sun-Flower	Linseed	Safflower	Soybean	Vernonia <sup>d</sup>	Cotton Seed	Coconut
Oleic	234 @15mm	7	58	7	25	22	14	25		24	
Linoleic	229 @16mm	4	20	3	66	16	75	51		42	7
Linolenic	231 @17mm	3	11			52	1	9			2
Eleostearic	170 @1mm	80									
Ricnoleic	227 @10mm			87							
Stearic	226 @10mm	1	2	1	2	4	4	4		4	6
Palmitic	210 @10mm	5	4	1	5	6	6	11		29	11
Myristic	190 @10mm			1						1	18
Lauric	170 @10mm										
Capric	152 @10mm										44
Caprylic	124 @10mm										6
Vernolic									80		6

<sup>a</sup>C H Hare, Anatomy of Paint, Journal of Protective Coatings, October 1989 Figures cited are approximate percentages only

<sup>b</sup>Chemical & Process Technology Encyclopedia, 1974

<sup>c</sup>Canola Council of America, Product Information, 1990

<sup>d</sup>S Dirlikov and M S Islam, Vernonia Oil A New Reactive Diluent, Modern Paint and Coatings, August 1990

<sup>e</sup>Federation Series on Coatings Technology, August 1974



Table 3-3 Composition of Normal Fatty Acids<sup>a</sup>

ACID	CARBON ATOMS	DOUBLE BONDS	FORMULA
Stearic	18	0	$\text{HOOC}(\text{CH}_2)_{16}\text{CH}_3$
Oleic	18	1	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$
Linoleic	18	2	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$
Linolenic	18	3	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$
Palmitic	16	0	$\text{HOOC}(\text{CH}_2)_{14}\text{CH}_3$
Myristic	14	0	$\text{HOOC}(\text{CH}_2)_{12}\text{CH}_3$
Lauric	12	0	$\text{HOOC}(\text{CH}_2)_{10}\text{CH}_3$
Capric	10	0	$\text{HOOC}(\text{CH}_2)_8\text{CH}_3$
Caprylic	8	0	$\text{HOOC}(\text{CH}_2)_6\text{CH}_3$
Eleostearic	18	3	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$
Ricinoleic	18	1	$\text{HOOC}(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CHOH}(\text{CH}_2)_5\text{CH}_3$

<sup>a</sup>Chemical and Process Technology Encyclopedia, 1974.

tung oil consists of 80 percent eleostearic acid, whereas soybean oil is made up of 51 percent linoleic acid.

The acid value in Table 3-1 indicates the amount of free fatty acids in an oil, expressed as the number of milligrams of potassium hydroxide required to neutralize the acids in 1 gram of oil.<sup>5</sup>

### 3.2 DRYING CLASSIFICATION

The double bonds in unsaturated fatty acids are chemically reactive sites and are the points at which oxygen reacts with an oil to produce drying.<sup>6</sup> Therefore, the degree of unsaturation of the fatty acid determines the drying properties of the oil. Vegetable oils are often classified as nondrying, semi-drying, or drying oils, with the first group containing a higher content of saturated fatty acids and the last group a higher content of unsaturated fatty acids.<sup>7</sup> The choice of oils for use in coatings is influenced by the drying properties, and this classification can be helpful in that decision.

Nondrying oils have low unsaturation or contain less than 20 percent of linoleic acid. Coconut, cottonseed, and castor oil are members of this group. Large quantities of these oils are consumed in edible products, and others are used in soaps or surface-active products.

Drying oils have greater unsaturation or greater quantities of fatty acids with higher unsaturation, such as linoleic acid or linolenic acid.<sup>8</sup> Oils in this group include linseed, tung, and dehydrated castor oil which are found in paints, varnishes, and other coatings.

Semi-drying oils are intermediate between the non-drying and drying oils in properties and contain about 40 to 60 percent linoleic acid.<sup>9</sup> Safflower, soybean, and sunflower oils are classified in this group, because they can be used in products of both classes after modifications. For example, soybean oil can be deodorized and inhibited with antioxidants to make an edible salad oil, or it may be modified to make a long oil alkyd performing much

like linseed oil.<sup>10</sup>

Semi-drying and drying oils were long used as binders in the protective-coating industry but have been largely replaced by synthetic binders in many of the coatings used now. The binder is the non-volatile resinous or resin-forming constituent of coating, responsible for forming the film.<sup>11</sup> The binder plus a solvent is referred to as the vehicle.

The term iodine value in Table 3-1 indicates the degree of unsaturation of an oil, and is expressed as the centigrams of iodine absorbed by one gram of oil under controlled conditions.<sup>12</sup> Usually oils with high iodine values have better drying properties, although this statement is not applicable when comparing conjugated with non-conjugated oils.<sup>13</sup> Conjugated double bonds are two or more double bonds which alternate with single bonds in an unsaturated compound (e.g.,  $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$ ). Non-conjugated double bonds occur when the unsaturated sites are separated by one or more additional methylene groups (e.g.,  $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ ).

### 3.3 VOLATILITY/PHOTOCHEMICAL REACTIVITY

Volatility is defined as the tendency of a solid or liquid material to pass into the vapor state at a given temperature. Experimentally, the volatility is determined by dividing the vapor pressure of a component by its mole fraction in the liquid or solid.<sup>14</sup> The vapor pressure of a substance (often expressed in millimeters of mercury, mm Hg) is the pressure characteristic at any given temperature of a vapor in equilibrium with its liquid or solid form.<sup>15</sup> Very little information relating to the determination of volatility (direct determination of vapor pressure for oils) was retrieved during the literature search and data gathering phase of this program. Vapor pressure information was obtained only for soybean oil. At a temperature of 254°C, soybean oil has a vapor pressure of 0.001 mm Hg. At a temperature of 308°C, soybean oil has a vapor pressure of 0.05 mm Hg.<sup>16</sup> The extrapolation of these vapor pressures to standard conditions (27°C) would yield no measurable vapor pressure at room temperature. Boiling points for the oils cannot be measured at atmospheric pressure,

since decomposition of the oil (as indicated by discoloration of the oil, charring, and ultimately evolution of smoke)\*\* occurs before the oil can actually boil. Therefore, the most direct indicators of volatility, vapor pressure and normal boiling point, although not directly available for the vegetable seed oils, obviously are such that one would not expect the oils to vaporize to any significant extent. Boiling points could be obtained for many of the fatty acids which constitute the major portion of the oil molecule. These fatty acid boiling points were determined under reduced pressure (typically 1 - 20 mm Hg rather than at 760 mm Hg which is atmospheric pressure) because decomposition is observed when the fatty acids are heated at atmospheric pressure.

The Glossary for Air Pollution Control of Industrial Coating Operations defines VOC as:

any organic compound which participates in atmospheric photochemical reactions; that is, any organic compound other than those which the Administrator designates as having negligible photochemical reactivity. VOC may be measured by a reference method, an equivalent method, an alternative method or by procedures specified under any subpart. A reference method, or an alternative method, however, may also measure nonreactive organic compounds. In such cases, an owner or operator may exclude the nonreactive organic compounds when determining compliance with a standard.<sup>17</sup>

This definition gives precedence to the analytical method specified for any specific standards under the New Source Performance Standards (NSPS) program. The definition presented in 40 CFR, parts 51 and 52, specifically identifies those organic compounds (all of which, except for methane and ethane, are halogenated) which the Agency has deemed of negligible reactivity. The Agency permits any emissions of these materials to be excluded from a measurement such as RM-24/24A of total volatiles. New materials are being added to the list of exempt compounds.

Vegetable seed oils are a VOC by this definition since the definition contains no

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\*\*Decomposition, of course, causes some portion of the oils to become airborne and available for photochemical reactions.

specific criteria pertaining directly to volatility, vapor pressure, number of carbon atoms, or boiling point.

### 3.4 THERMAL STABILITY

No oil decomposition temperatures (the point at which oils start to decompose upon heating) were found from the literature search. However, the smoke points of four of the vegetable oils have been determined and are found in Table 3-1. Bailey's provides the following definitions regarding thermal stability.

The smoke, fire, and flash points of a fatty material are measures of its thermal stability when heated in contact with air. The smoke point is the temperature at which smoking is first detected in a laboratory apparatus protected from drafts and provided with special illumination. The temperature at which the material smokes freely is usually somewhat higher. The flash point is the temperature at which the volatile products are evolved at such a rate that they are capable of being ignited but not of supporting combustion. The fire point is the temperature at which the volatile products will support continued combustion.<sup>18</sup>

Impurities such as free fatty acids lower the smoke point of the oil drastically.<sup>19</sup> Canadian government specifications require that a good frying oil have a smoke point above 200°C.<sup>20</sup> Clearly, any event (e.g. heating) which causes the oil to smoke results in airborne decomposition products that are available for photochemical reactions.

### 3.5 INDIVIDUAL OILS

#### 3.5.1 Canola Oil

Canola seed is bred from rapeseed, a member of the mustard family. Most of the world's supply of canola oil comes from Canada and Europe. Research is being performed to solve production problems in order to increase yield since demand surpasses supply.<sup>21</sup> The

oil is composed of 58 percent oleic acid which makes it lower in saturated fat than coconut, soybean or any of the other oils.<sup>22</sup> Therefore, there is a large demand for canola oil from health-conscious consumers. Canola consumption has risen from 100,000 lbs in 1986 to 500 million lbs in 1989, and it is expected to grow 7 percent each year to 700 million lbs by 1994.<sup>23</sup> Even with the higher price in the grocery store, \$3.99 for 16 oz. canola oil versus \$0.89 for 16 oz. of vegetable (unspecified) oil, sales are increasing.<sup>24</sup> Canola oil is, however, used more in food products than in coatings.

### 3.5.2 Castor Oil

Castor oil is extracted from the seed of the castor plant which is grown commercially in Brazil, India, and in some of the warmer sections of the United States. The seeds generally contain about 45 percent oil.<sup>25</sup> Not only is the oil itself useful in a variety of compositions, but it is capable of undergoing several kinds of chemical transformations (such as dehydration) by which it is converted into useful derivatives. Castor oil differs from other vegetable oils by having higher viscosity, greater solubility in alcohol, and lesser solubility in petroleum solvents.<sup>26</sup> These properties are important for its uses in paint, varnish, plasticizers, hydraulic fluids, and cosmetics.

Dehydrated castor oil is among the most valuable drying oils for coatings. It dries faster, heat-bodies (thickens when heated) faster, has equal color retention and imparts superior film toughness to alkyds than soybean oil.<sup>27</sup> However, usage of castor oil is restricted by its somewhat higher cost (\$0.405/lb as compared to \$0.25/lb for soybean oil).<sup>28</sup>

### 3.5.3 Coconut Oil

Coconut oil is obtained from copra, the dried, broken kernels of coconuts; copra contains about 65 percent oil.<sup>29</sup> With an average iodine value of 10 or less and only 9 percent unsaturated acids, coconut oil is more stable to oxygen and heat than any other natural oil.<sup>30</sup> Because of this stability, alkyd coating resins that contain coconut oil are

permanently flexible and are highly color retentive, even when baked at high temperatures.<sup>31</sup>

Coconut oil is relatively resistant to the type of rancidity caused by oxidation at ordinary temperatures, but it is susceptible to a type of rancidity caused by microorganisms, especially various molds.<sup>32</sup> Therefore, food products and other materials containing coconut oil and moisture are subject to this type of spoilage. Even so, this oil is used for food products, soaps, and coatings. However, due to its high saturated fat levels, its use in food products is declining.<sup>33</sup>

#### 3.5.4 Cottonseed Oil

Cottonseed oil is extracted from the seed of the cotton plant, which is grown primarily in the United States, India, U.S.S.R, Brazil, China, and Egypt.<sup>34</sup> Practically all of the crude cottonseed oil produced in this country is refined for use in edible products such as shortening, margarine, and cooking oils.<sup>35</sup> Cottonseed oil demand is stimulated by its amenability to many frying applications.<sup>36</sup> However, due to its low unsaturation it could also be used as a lower cost substitute for coconut oil in color retentive baking alkyds. Alkyds made with cottonseed oil have better color retention than those made with soybean and safflower oils but are inferior in gloss and toughness.<sup>37</sup>

#### 3.5.5 Linseed Oil

Linseed oil is a low-melting oil, is slightly less viscous than most vegetable oils, and has a high iodine value which reflects the high degree of unsaturation of its fatty acids. Linseed oil is obtained from flaxseed, which averages about 35 percent oil content.<sup>38</sup> Linseed oil is not well suited for use as an edible fat, but it is used in the manufacture of paints (particularly artists' paints), varnishes, and printing inks. It is the sole binder in oil house paint in which the binder is usually a blend of thin linseed oil, raw or refined, with heat-bodied linseed oil.<sup>39</sup> A thin, alkali refined linseed oil is also used for alkyd paints where fast drying is important and good color retention is not required.

One property of linseed oil that must be considered when choosing a linseed oil paint is "after-yellowing." Linolenic acid yellows more than other fatty acids and largely governs the yellowing of oils. Since linseed oil contains the highest proportion (52 percent) of this acid, it yellows more than other oils, thereby causing a yellow tint to linseed oil-based paints.<sup>40</sup>

A disadvantage of the use of linseed oil-based paints is its high susceptibility to mildew. Mildew, a fungus which flourishes in damp environments, is a common cause of the discoloration and degeneration of house paint and unfinished wood. Many paints contain mildewcides which serve to prevent and cure mildew problems.<sup>41</sup>

The demand for fats and oils for all uses will grow 1.8 percent per year to about 21 billion pounds in 1994, and growth in the use of linseed oil in coatings and inks will continue.<sup>42</sup>

### 3.5.6 Safflower Oil

The safflower plant, from which safflower oil is obtained, is grown in Africa, and the Middle East, as well as in the western portion of the United States. The seeds contain about 30 percent oil. Safflower oil is used in some food products but is used more frequently as a drying oil in coatings. The oil falls between soybean oil and linseed oil in total unsaturation and in price. As for its drying properties, safflower oil is closer to linseed than to soybean. Unless modified, safflower oil does not dry fast enough for use in house paints.<sup>43</sup>

Approximately 75 percent of the fatty acids of safflower oil are linoleic and only one percent are linolenic, which compares with 9 percent linolenic in soybean oil. Because of this unique composition, safflower oil dries faster and yellows less than soybean oil coatings.<sup>44</sup>

### 3.5.7 Soybean Oil

Soybean oil, also called soya oil, is extracted from the seeds of soybean plants which



are grown in many areas of the United States and South America. In fact, the United States is the world's leading producer of soybeans, which is the American farmer's second-largest cash crop.<sup>45</sup> Crude soybean oil usually contains no more than 1.5 percent free fatty acids, often less than 0.5 percent, and from 1.5 to 4 percent other impurities.<sup>46</sup> These constituents are removed from the oil during refining and degumming processes. Refined soybean oil consists primarily of the triglycerides of oleic, linoleic, linolenic, saturated acids, and about 0.8 percent impurities (referred to as unsaponifiable material).<sup>47</sup> Most varieties of oil seeds contain from 18 to 22 percent oil.<sup>48</sup>

The soybean is an annual crop that is well suited to mechanized planting, cultivation, and harvesting. Varieties have been developed to suit various climates and soils, and new varieties continue to be developed. The price of soybeans remains one of the lowest of vegetable oils (about \$0.25 per pound of crude).<sup>49</sup> Because of the large number of varieties of soybeans grown and the diversity of soils and climate in which they can be successfully cultivated, the physical and chemical properties of soybean oils will vary. For example, the iodine value of soybean oil varies with the plant variety and also varies within the same variety grown in different locations and in different years.<sup>50</sup> In one study in which samples of cultivated soybeans were extracted under uniform conditions in the laboratory, oils having iodine values ranging from 99.6 to 143.2 were obtained. These samples represented ten varieties grown in several locations in different crop years.<sup>51</sup> Oils produced commercially tend to vary less because of the blending of different lots of seeds that takes place in ordinary commercial handling and milling. One comparison of 87 soybean oil samples produced commercially showed a range in iodine values from 129.3 to 136.7.<sup>52</sup> These variations may be partially due to the variability in weather conditions such as temperature and humidity which affects the metabolic processes involved in the biosynthesis of lipids (fats) in the growing seed.<sup>53,54</sup> The moisture content of soybeans at the time of harvesting depends a great deal upon the weather and the maturity of the beans, and it is an important factor in determination of the grade of soybeans.<sup>55</sup>

The principal uses of soybean oil are in food products and as an ingredient in paints,

inks, and other drying oil products. Soybean oil's low saturated fat content and lack of cholesterol have made it a popular choice for food manufacturers and fast food chains.<sup>56,57</sup>

Soybean oil is the most widely consumed of the vegetable oils with a projected growth rate of 1.9 percent per year through 1994.<sup>58</sup>

Because of the semi-drying nature of soybean oil, no paints are made from straight soybean oil. However, alkyds (oil based paints) made from soybean oil have good drying properties, and it is used more than any other oil for making alkyd resins found in architectural and industrial coatings.<sup>59</sup> Soya alkyds are also widely employed as binders for interior and exterior air-drying enamels, marine paints, and alkyd type house paints.<sup>60</sup>

Soya alkyds are classified as color retentive, and satisfy the color requirements of the majority of white and light colored top coats, both air dried and baked.<sup>61</sup> There is also evidence that colored inks made with soybean oil have greater color rendition (brightness) than inks made without it.<sup>62</sup> News inks made from soybean oil also resist rub-off better than conventional inks.<sup>63</sup> For these reasons, there has been an increase in the use of soybean oil in the printing industry.

In general, paints and inks contain solvents and/or petroleum distillates which emit VOC's to the atmosphere. Based on Method 24 (see Section 6.0), Flint Ink Corporation found that the substitution of a mixture of soybean oil and corn oil for the middle petroleum distillates in a sheetfed offset ink greatly reduced the VOC content.<sup>64</sup> We expect the use of soybean and perhaps other vegetable oils in place of the more volatile petroleum distillates to reduce ozone formation since their slower evaporation rate greatly offsets the oxidation reaction that releases some unquantified amount of light hydrocarbons (Section 5.0). The Hazardous Waste Research and Information Center in Illinois is carrying out a research project entitled "Toxic Substance Reduction for Sheetfed Offset Printers" to determine the waste reduction advantages of substituting soybean oil for petroleum based inks and organic solvent based cleaners.

A benefit of using soybean oil in coatings is that it is a renewable, domestically produced and processed product. The fact that soybeans can be planted and harvested year after year is an advantage. Since soybeans are commonly used in food products, toxicity does not appear to be a problem. Disposal of soybean-based products could also be considered less problematic than petroleum-based products since the oils appear to be more readily biodegradable.<sup>65</sup>

#### 3.5.8 Sunflower Oil

Sunflower oil, a light yellow oil well suited for use as a salad and cooking oil, is obtained from the sunflower seed plant that is grown primarily in Europe and the U.S.S.R.<sup>66</sup> The oil content of the seed may average about 29 percent.<sup>67</sup> Total unsaturation of the oil is comparable with that of soybean oil, but the linolenic acid found in soybean oil is lacking in sunflower oil. Sunflower oil is classified as a semi-drying oil and is used in the manufacturing of oil-modified alkyd resins and similar products.<sup>68</sup> Like soybean oil, the iodine value and composition of sunflower oil are influenced by the plant variety, temperature, soil fertility and moisture supply. Oils differing widely from each other in iodine value usually differ in the ratio of linoleic to oleic acid rather than in any large difference in total content of unsaturated acids.<sup>69</sup>

#### 3.5.9 Tung Oil

Tung oil, also known as China wood oil, was originally obtained from China but is now grown in the southern United States. Tung oil is a highly unsaturated oil with a viscosity considerably higher than that of linseed oil. Since tung oil has laxative if not poisonous properties, it is not considered edible.<sup>70</sup> However, since tung oil is classified as a drying oil it is utilized in varnishes, enamels, and other products in which the drying quality of the oil is important. Tung oil works well in combination with relatively inexpensive resins and, compared with nonconjugated oils, tends to confer superior water resistance, alkali resistance, hardness, and durability on the products in which it is used.<sup>71</sup>

Eleostearic acid is the principal fatty acid in tung oil, and it is the chemical nature of this acid that differentiates tung oil from other drying oils. Eleostearic acid is an isomer of linolenic acid, and it has its three double bonds in the conjugated relationship with each other.<sup>72</sup> This conjugated unsaturation is responsible for the fact that tung oil thickens and gels more readily than other oils when heated. The very rapid bodying of tung oil precludes its use as a large part of the oil in alkyd resins.<sup>73</sup>

#### 3.5.10 Vernonia Oil

Vernonia oil is extracted from the vernonia plant, a new potential oil seed crop grown in Africa, Asia, Central America, and in the southwest United States. Vernonia seeds contain about 42 percent oil in contrast to soybean seeds, which contain 17 to 18 percent oil.<sup>74</sup> Vernonia oil contains predominately (about 80 percent) trivernolin, a triglyceride of vernolic acid. A unique property of this oil is its homogeneous molecular structure consisting primarily of identical triglyceride molecules with three equal vernolic acid residues. In contrast, all other vegetable oils consist of a heterogeneous mixture of triglycerides with different fatty acid residues.<sup>75</sup>

Vernonia oil is a transparent homogeneous liquid at room temperature with low viscosity and excellent solubility in numerous organic solvents, diluents, and paints. Due to these properties, vernonia oil is being considered as a reactive diluent (reduces viscosity like a conventional solvent but also reacts with the coating resin in the drying process) for high-solids alkyd, epoxy, and epoxy-ester coating formulations by replacing conventional solvents which ultimately are released as VOC emissions.<sup>76,77</sup>



#### 4.0 PROCESSING AND REFINING VEGETABLE SEED OILS

The following description of the processing and refining procedures may vary for different vegetable seeds, but in general, the steps are similar. In order to extract oil from vegetable seeds, the seeds are first cleaned, dried, cooled, and transferred to tempering bins to allow the moisture within the seeds to redistribute itself.<sup>78</sup> The seeds are cracked, dehulled, and rolled into flakes until the oil cells are exposed. These flakes are then extracted with the solvent hexane to remove fats. The solvent is removed, and the flakes are toasted with steam, dried, cooled, and ground into meal.<sup>79</sup> The remaining solvent-oil mixture is distilled to separate the two into solvent and crude vegetable oil.

In its crude state, vegetable seed oil contains, besides the triglycerides, a number of impurities such as gums, phosphatides, free fatty acids, pigments, and traces of oxidation products from oil degradation.<sup>80</sup> The purpose of refining oils is to remove these unwanted materials to attain quality standards for end-use products, whether they be food or non-food products. Degumming is an optional first step in purification in which water is added to the oil to dissolve the hydratable phosphatides, and the mixture is then separated by centrifugation.<sup>81,82</sup> The next step is to neutralize the free fatty acids with alkali and to separate the resultant soap. This process is referred to as saponification; the term saponification number found in Table 3-1 is defined as the number of milligrams of potassium hydroxide required to saponify 1 gram of fat.<sup>83</sup> The next step is to react the oil with an activated bleaching clay to remove pigments and oxidation products; the last is to deodorize by steam distillation at reduced pressure. This treatment removes most of the remaining free fatty acids, some color bodies, and some unwanted flavor.<sup>84</sup> Vegetable oils used in coatings generally do not require the deodorization step, only refining and bleaching.<sup>85</sup> After deodorization, the oil can be made more viscous by injecting air into the oil at elevated temperatures to partially oxidize the oil to create bodied or blown oil.<sup>86</sup>



## 5.0 DRYING/CURING PROCESSES

### 5.1 OXIDATION

Oxidation is the reaction of oxygen with another substance in which electrons are transferred. Autoxidation, the oxidation of vegetable oils with the oxygen as present in the atmosphere, affects the oils in various ways. Fats and oils intended for food can become rancid due to oxidation if not handled and stored properly. However, the drying of paint films is dependent on the oxidation process. Most coatings, in spite of their apparent diversity, dry by much the same oxidizing mechanism, whether they are alkyds, epoxy esters, urethane alkyds, or oil-based coatings.<sup>87</sup> All are based on drying oils, the naturally occurring triglyceride esters of certain unsaturated fatty acids bearing multiple double bonds.<sup>88</sup>

There are a number of factors that affect the oxidation process.<sup>89</sup>

- The reaction is accelerated by light.
- Film thickness influences oxidation rate, because oil oxidizes more rapidly in shallow layers than in deep layers.
- Temperature influences reaction rate. For example, heat usually accelerates oxidation.
- The rate of oxidation is greatly dependent upon unsaturation and the structure of the fatty acids present in the oil. Unsaturated fats are more susceptible to oxidation than saturated fats.
- The presence or absence of antioxidants or prooxidants will affect oxidation. Antioxidants, which sometimes occur naturally in vegetable oils, delay or reduce the oxidation process. Prooxidants accelerate the reaction, and are often added in the form of driers. Driers are oil-soluble metallic compounds such as cobalt or manganese deliberately added to oils for the purpose of accelerating the oxidation and drying of oils used in coatings.
- The fewer impurities in the oil, the faster the oxidation and drying processes.<sup>90</sup>



## 5.2 CHEMICAL REACTIONS OF THE DRYING/CURING PROCESS

Since the drying/curing processes of oils are generally described in terms of coatings, the following process description reflects oils in coatings, not oils alone.

Autoxidation of oils is the basis for the drying/curing of coatings. Drying is defined as the polymerization of the glycerides of unsaturated vegetable oils induced by exposure to air or oxygen.<sup>91</sup> Curing is the conversion of a raw product to a finished and useful condition, usually by application of heat and/or chemicals which induce physicochemical changes.<sup>92</sup> The mechanism, while not fully understood, involves the reaction of oxygen with the double bonds or active methylene groups in the oil or resin medium. The reaction usually entails a free-radical mechanism and is initiated by heat, light, metallic catalysts, or free-radical generators.<sup>93</sup> Autoxidation may be thought of as being analogous to addition polymerization.<sup>94</sup>

In autoxidation, oxygen attacks the fatty acid chains at or near the double bonds. Non-conjugated fatty acids are thought to first undergo a rearrangement of their bonding to give conjugated forms. This oxygen attack involves the formation of hydroperoxides ( $\text{ROOH}$ , where R is a fatty acid chain) that subsequently break down to form free radicals ( $\text{RO}\cdot$ ). These free radicals readily attack other fatty acid chains at the methylene group between the two double bonds, producing other free radicals ( $\text{R}\cdot$ ), and allowing bond rearrangement.<sup>95</sup>

With the conjugated double bonds available, drying proceeds as it does with conjugated acids. Oxygen attacks the double bonds to form peroxy radicals ( $\text{R-O-O}\cdot$ ), which interact to form polyperoxides (long chains of fatty acid molecules linked together by  $-\text{O-O}-$  groups), or which may react with other fatty acids to form large, complex, crosslinked materials.<sup>96</sup> The radicals can also decompose, leading to the evolution of volatile organics such as aldehydes, ketones and alcohols.<sup>97</sup>

### 5.3 PRODUCTS OF COATING OXIDATION

Emissions from the formation of a coating film result from:

- (1) evaporation of the solvent portion of the coating,<sup>98</sup> and
- (2) reaction by-products emitted during the chemical reaction that takes place in coating films at cure temperatures.<sup>99</sup>

The latter are denoted cure volatiles, and include a variety of compounds such as aldehydes, ketones, acids, water, carbon dioxide, hydrogen, polymerized fats, epoxides, and peroxides.<sup>100</sup> If heat is not applied, as with many inks, some of these compounds such as aldehydes remain in the film instead of volatilizing.<sup>101</sup> A more detailed discussion of the oxidation products of vegetable oils is found in Section 6.0.



## 6.0 VOC TEST PROCEDURES AND FINDINGS

The methodology chosen to evaluate the impact of a policy decision declaring soybean oil exempt from regulation on the Agency's program for coatings was to determine the VOC content of the oil with the Agency's analytical methods for measuring the VOC content of coatings and inks.

EPA's Reference Method 24 is applicable to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings (solvent-borne and waterborne). The quantity of VOC in surface coatings is defined by the results of Method 24. Using the test protocol for Method 24, samples are weighed and then heated at  $110 \pm 5^{\circ}\text{C}$  for one hour. The samples are weighed again after heating. Loss in weight represents evolution of volatile material which would include water, VOC and non-reactive (exempt) volatile compounds. Procedures are included within Method 24 to determine water content either by direct injection into a gas chromatograph or by Karl Fischer titration either to a colorimetric end point or to a potentiometric end point. Coating density and solids content may also be determined by procedures included in Method 24. In commercial and regulatory applications, the pounds of VOC per gallon of coating less water and exempt compounds is calculated from the measured loss of weight and the exempt compound and water content of the coating.

EPA's Reference Method 24A is applicable to the determination of VOC content and density of solvent-borne (solvent-reducible) printing inks and related coatings. The VOC in printing inks and related coatings is defined by the results of Method 24A. For Method 24A, a sample is heated at  $120 \pm 2^{\circ}\text{C}$  for 24 hours in a forced draft oven, or the sample may be heated for a shorter period of time in a vacuum oven. Method 24A also incorporates procedures for the determination of coating density and solvent density, but procedures for the determination of water content are not required in Method 24A since the method applies to solvent-borne printing inks and related coatings.

The EPA reference methods provide a single number which is characteristic of the weight percent VOC. Other methods found in the literature have been applied to characterize, qualitatively, the VOC's which are emitted from vegetable oils under certain conditions. The next sections will discuss the results of this work, and results from the EPA test methods.

## 6.1 TESTS CONDUCTED BY THE PAINT RESEARCH ASSOCIATION

Long ago, the Research Association of British Paint, Colour, and Varnish Manufacturers measured water, carbon dioxide, volatile acids, and aldehydes evolved from the drying process (autoxidation) of oil films at ambient temperatures.<sup>102</sup> To determine the nature of the volatile compounds which were emitted in the course of the drying process, the British chemists coated the interiors of bottles with a thin film of oil. A stream of air was then passed through six bottles in series for seven days so that acidic volatile products which were formed could be collected in a solution of sodium bicarbonate and characterized. The British chemists found that the main acidic compound which was formed from linseed oil was formic acid. The amount of volatile products evolved from oil films after seven days of aging in the laboratory could account for a significant degradation of the acid portion of the triglyceride molecule. Reaction in the molecule appeared to begin by cleavage at or adjacent to a double bond, followed by progressive degradation along the chain with release of volatile acids and carbon dioxide. The total amount of volatile materials released varied with the type of oil tested. These experiments were performed approximately forty years ago, prior to the availability of now common chromatographic techniques. Not all hydrocarbons were characterized. Aldehydes and acids formed solid derivatives which could be characterized by melting point and other physical properties.

Since the oxidation is a surface phenomenon, the oxidation process is accelerated when more surface area is created for the oils. The British studies, using oils in a thin film at room temperature, accelerated the autoxidation process. Industrial applications which require spraying of oil create an aerosol of the oil which dramatically increases the surface area over that of bulk oil. Autoxidation processes are accelerated in these spraying applications,

thereby enhancing the production of volatile oxidation products.

## 6.2 APPLICATION OF GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUES

Autoxidation of vegetable seed oils with the resulting formation of odors and flavors has been studied extensively for many years. Oil manufacturers, oil chemists, and chemists in the areas of flavors and fragrances have extensively studied the evolution of volatile material from oils under various conditions. Autoxidation of oils proceeds slowly under room temperature conditions, but the reactions still occur: oil becomes yellow and darkens under prolonged storage. If the period of storage is long enough or if conditions are favorable for accelerated oxidation, the oil becomes rancid. In the last ten to twenty years, the powerful combined techniques of gas chromatography and mass spectrometry have been available to characterize the products obtained from the oxidation of oils under various conditions. For the most part, investigators have been concerned with the oxidation of oils used in cooking applications, since heat accelerates the oxidation process and volatile decomposition products formed in oils used in cooking can affect the taste and smell of foods cooked in the oil. No formal reference test methodology has been available for these applications: investigators have developed their own methodology to meet their needs in characterizing the volatile materials emitted from the oils. Quantitative data have not been obtained because the decomposition process in heated oils is an ongoing process. Oxidation reactions proceed as long as the oil is heated and sites of reaction (double bonds) remain in the triglyceride molecule. Thus, volatile decomposition products will continue to form until no more reaction sites are available and the oil is decomposed to a tar.

While the primary concern has been with the cooking process, studies have been performed at room temperature. In order to identify the volatiles formed during the storage of soybean oil, a time versus volatile decomposition study was performed on oil aged under normal laboratory conditions.<sup>103</sup> The experiment involved vacuum stripping of volatile materials from the oils over a period of five to six hours. The volatile materials stripped

from the oils were collected cryogenically, the cryotrap was heated, and the ultimate analysis was performed by gas chromatography/mass spectrometry. The investigators found that hydrocarbons and aldehydes were the principal volatile compounds which resulted from soybean autoxidation by comparing fresh oil with oils which had been allowed to sit under laboratory conditions for a period of six weeks. The oil which had been allowed to sit exhibited larger quantities of the hydrocarbons and aldehydes, but new compounds were not formed as the oil aged over the longer time period.

Most other studies available in the published literature have been performed on the headspace generated above heated oils, with qualitative analysis of the organic compounds emitted from the oil under these conditions.<sup>104,105</sup> The compounds which are observed are characteristic of the oxidation/decomposition of a fatty acid triglyceride and include hydrocarbons of various lengths and conditions of saturation, as well as aldehydes and ketones. In most cases, volatiles were generated in the headspace above oils heated to 180°C, since 180°C is the temperature used in cooking applications. In general, fresh oil samples produce few chromatographic peaks of low intensity, whereas the oils which had been aged for varying periods of time produced relatively more volatile materials.<sup>106</sup> In addition, the volatile compounds identified were those expected from the autoxidation of the unsaturated fatty acid components of each of the vegetable seed oils.

### 6.3 VOC TEST RESULTS

The Emissions Measurement Branch (EMB) conducted RM-24 and RM-24A testing (Appendix i) on various vegetable seed oils for the purpose of this study at the Research Triangle Park laboratories. For the Method 24 testing, the sample was weighed, heated in a forced draft oven at 110°C for 1 hour, then re-weighed. For Method 24A, the heating time was 24 hours at 120°C in a forced draft oven. Alternatively, for Method 24A, the heating may take place for 0.5 hour in a vacuum oven, but the atmospheric pressure technique was used for these samples. Test procedures shown in Appendix i were followed, with the exceptions that no solvent was added to the sample and no moisture determinations were

performed.

Method 24 testing was performed on two samples of soybean oil purchased from the grocery store (Food Club vegetable oil, Pittsburgh, PA; and Wesson oil, Durham, NC). The results of the Method 24 determinations, shown in Appendix ii, showed that these oils did not exhibit weight loss, indicating that these samples contained no VOC.

Method 24A testing was performed for eleven vegetable oil samples representing seven different oils, shown in Table 6-1. The vernonia oil was supplied by Stoil Dirlikov of the Coatings Research Institute at Eastern Michigan University. Other oil samples were supplied by David Ailor, Director of Regulatory Affairs, of the National Oilseed Processors Association (NOPA). The results of the RM-24A testing are shown in Appendix iii, and all of the test results are summarized in Table 6-1. Table 6-1 shows that all of the samples except for vernonia oil exhibited a gain in weight ranging from 0.01 percent to 3.56 percent. In addition, under the testing conditions, several of the oils solidified or crystallized, indicative of a change in physical condition and/or chemical composition. A solid structure is indicative of cross-linking between molecules or components of molecules, or oxidation with a concomitant gain in weight. However, there are multiple oxidation reactions which could occur, ranging from the formation of peroxides to formation of alcohols, aldehydes, ketones, and acids. Where the oils have changed structure, it is also possible that volatile materials are entrained in the solid oils, trapped beneath the surface film. These volatile materials will eventually permeate the surface film and be emitted from the oil, but the timetable for this permeation process may be hours or days. The oils were not homogeneous in composition prior to the heating process, so the number of potential reactions is so large that it is not possible to assess accurately how much oxidation has occurred in order to account quantitatively for the gain in weight observed under the test conditions of Method 24A. Further, this inability to determine the weight gain attributable to oxidation precludes our ability to judge the amount of VOC evolved by the oil during the fractionation - oxidation reaction. What did seem clear is that enforcement of air pollution regulations using RM-24 and 24A would not falsely jeopardize a source using coatings with a vegetable oil constituent.



Table 6-1 Test Results\*\*\*

	EPA RM-24A RESULTS (% VOC or Average weight loss)	EPA RM-24 RESULTS (% VOC or Average weight loss)
Canola	-0.87	
Castor		
Coconut		
Cottonseed	-0.01, -0.63	
Linseed <sup>d</sup>	-2.14, -2.30	
Safflower		
Soybean	-0.51, -0.66, -1.25	0, +0.1, -0.1, -0.3
Sunflower	-0.62	
Tung <sup>e</sup>	-3.56	
Vernonia <sup>c</sup>	+3.54	

<sup>d</sup>solidified ; <sup>b</sup>crystallized ; <sup>c</sup>dried -

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\*\*\* The results include the organics and moisture. Different samples of each vegetable oil were used for each test.

## 7.0 IMPACT OF TEST RESULTS ON TEST METHODS AND REGULATIONS

The results obtained by the application of Method 24 to soybean oil demonstrate that this oil and, by extrapolation, other vegetable seed oils do not contain VOC. Since the literature provides no obvious evidence that soybean oil can be distinguished from other vegetable seed oils in any significant way from the standpoint of volatility or photoreactivity, the observations have been extended to the other vegetable seed oils. Thus, the presence of vegetable seed oils in coatings should neither mask nor interfere significantly with Method 24 testing of coatings. Measurement of VOC content of a coating by RM-24A may yield an erroneous value due to possible weight gain by the oil in the coating under the conditions of the test. However, the degree of the error is both small and will provide a margin of safety to the source since it would indicate less VOC than what is actually emitted. Therefore, there should be no significant impact on any of the coating regulatory compliance programs.

It should be noted, however, that this conclusion is not the same as concluding that vegetable oils do not contribute to ozone formation in the troposphere. RM-24 and RM-24A test conditions do not subject the oils to the temperature used in frying applications: a temperature of 180°C and atmospheric pressure is used in most frying applications, although some commercial frying is performed under pressure. Analytical results reported in the literature show that under the temperature conditions used for frying with soybean oil, VOC's such as hydrocarbons and oxygenated compounds are emitted to the atmosphere.<sup>107</sup> Since those VOC's are formed as a result of the temperature-catalyzed oxidation/decomposition of the fatty acid triglycerides which make up the oils, the decomposition process occurs at an accelerated rate as long as the oils are subjected to the elevated temperature and sites of unsaturation remain in the fatty acid carbon chains. Also, when food (mostly complex carbohydrates) is cooked at temperatures of 180°C in heated oil, the composition of the food is changed and volatile compounds are emitted from the food. This evolution of volatile compounds is evidenced by the odors when foods are cooked. Thus, cooking food also contributes to VOC emissions, although the magnitude of the contribution is unknown.

Therefore, although the vegetable seed oils themselves contain no VOC's when analyzed by Method 24 or Method 24A, the oils are precursors of VOC which are formed very slowly under conditions of standard temperature and at an accelerated rate under elevated temperature. The oxidation/decomposition reactions are also accelerated when the oil is present as an aerosol or mist, since a far greater surface area is created.

The only way to determine the volatile organic compound emissions from a deep fat frying operation would be to perform a stack test in which the emissions are speciated and quantified. The results, however, would be controversial. Aerosol oils, for example, would be measured as particulate matter. In as much as the oxidation, would the entire mass be considered VOC? Obviously it should not be, but what portion should be appropriately tagged for future cleavage? Clearly, such testing would yield a conservative estimate of VOC since the contribution of airborne oxidation of soybean oil to the formation of ozone precursors is not instantaneous.

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## APPENDICES

### Appendix i

#### VOC Test Methods

EPA Reference Method 24  
EPA Reference Method 24a  
(40 CFR Ch. 1, Pt. 60. App. A, 7-1-90 Edition)

ASTM D2369  
ASTM D4017  
ASTM D3792  
(Annual Book of ASTM Standards, Vol 06.01, 1987)

### Appendix ii

#### EPA RM-24 Test Results

### Appendix iii

#### EPA RM-24A Test Results

### Appendix iv

#### Frying Operations References



## APPENDIX i



**METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS**

**1. Applicability and Principle**

1.1 **Applicability.** This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 **Principle.** Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

**2. Applicable Standard Methods**

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475-80 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see § 60.17).

2.2 ASTM D2369-81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see § 60.17).

2.3 ASTM D3792-79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see § 60.17).

2.4 ASTM D4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see § 60.17).

**3. Procedure**

3.1 **Volatile Matter Content.** Use the procedure in ASTM D2369-81 (incorporated by reference—see § 60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W<sub>1</sub> = Weight of dish and sample before heating, g.

W<sub>2</sub> = Weight of dish and sample after heating, g.

W<sub>s</sub> = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in Section 4.3 is met. Calculate the weight fraction of the volatile matter (W<sub>v</sub>) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_s} \quad \text{Eq. 24-1}$$

Record the arithmetic average ( $\bar{W}_v$ ).

3.2 **Water Content.** For waterborne (water reducible) coatings only, determine the weight fraction of water (W<sub>w</sub>) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see § 60.17.) A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in Section 4.3 is met. Record the arithmetic average ( $\bar{W}_w$ ).

3.3 **Coating Density.** Determine the density (D, kg/liter) of the surface coating using the procedure in ASTM D1475-80 (Reapproved 1980) (incorporated by reference—see § 60.17).

Run duplicate sets of determinations for each coating until the criterion in Section 4.3 is met. Record the arithmetic average ( $\bar{D}$ ).

3.4 **Solids Content.** Determine the volume fraction (V<sub>s</sub>) solids of the coating by calculation using the manufacturer's formulation.

**4. Data Validation Procedure**

4.1 **Summary.** The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 **Analytical Precision Statements.** The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W <sub>v</sub> .....	1.5 pct W <sub>v</sub> .....	4.7 pct W <sub>v</sub> .....
Water content, W <sub>w</sub> .....	2.9 pct W <sub>w</sub> .....	7.5 pct W <sub>w</sub> .....
Density, D, .....	0.001 kg/liter.....	0.008 kg/liter.....

4.3 **Sample Analysis Criteria.** For W<sub>v</sub> and W<sub>w</sub>, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D, run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision

statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD-13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropriate between-laboratory precision value to the measured mean value for that parameter. For  $W_v$  and  $D_v$ , use the lower confidence limits, and for  $W_s$ , use the upper confidence limit. Because  $V_v$  is calculated, there is no adjustment for the parameter.

#### 5. Calculations

##### 5.1 Nonaqueous Volatile Matter.

##### 5.1.1 Solvent-borne Coatings.

$$W_v = W_s \quad \text{Eq. 24-2}$$

Where:

$W_v$  = Weight fraction nonaqueous volatile matter, g/g.

##### 5.1.2 Waterborne Coatings.

$$W_v = W_s - W_w \quad \text{Eq. 24-3}$$

##### 5.2 Weight Fraction Solids.

$$W_s = 1 - W_v \quad \text{Eq. 24-4}$$

Where:

$W_s$  = Weight solids, g/g.

#### METHOD 24A—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF PRINTING INKS AND RELATED COATINGS

##### 1. Applicability and Principle

1.1 Applicability. This method applies to the determination of the volatile organic compound (VOC) content and density of solvent-borne (solvent reducible) printing inks or related coatings.

1.2 Principle. Separate procedures are used to determine the VOC weight fraction and density of the coating and the density of the solvent in the coating. The VOC weight fraction is determined by measuring the weight loss of a known sample quantity which has been heated for a specified length of time at a specified temperature. The density of both the coating and solvent are measured by a standard procedure. From this information, the VOC volume fraction is calculated.

#### 2. Procedure

##### 2.1 Weight Fraction VOC.

##### 2.1.1 Apparatus.

2.1.1.1 Weighing Dishes. Aluminum foil 58 mm in diameter by 18 mm high, with a flat bottom. There must be at least three weighing dishes per sample.

##### 2.1.1.2 Disposable Syringe, 5 ml.

2.1.1.3 Analytical Balance. To measure to within 0.1 mg.

2.1.1.4 Oven. Vacuum oven capable of maintaining a temperature of  $120 \pm 2^\circ\text{C}$  and an absolute pressure of  $510 \pm 51$  mm Hg for 4 hours. Alternatively, a forced draft oven capable of maintaining a temperature of  $120 \pm 2^\circ\text{C}$  for 24 hours.

2.1.2 Analysis. Shake or mix the sample thoroughly to assure that all the solids are completely suspended. Label and weigh to the nearest 0.1 mg a weighing dish and record this weight ( $M_d$ ).

Using a 5-ml syringe without a needle remove a sample of the coating. Weigh the syringe and sample to the nearest 0.1 mg and record this weight ( $M_{s+n}$ ). Transfer 1 to 3 g of the sample to the tared weighing dish. Reweigh the syringe and sample to the nearest 0.1 mg and record this weight ( $M_{s-n}$ ). Heat the weighing dish and sample in a vacuum oven at an absolute pressure of  $510 \pm 51$  mm Hg and a temperature of  $120 \pm 2^\circ\text{C}$  for 4 hours. Alternatively, heat the weighing dish and sample in a forced draft oven at a temperature of  $120 \pm 2^\circ\text{C}$  for 24 hours. After the weighing dish has cooled, reweigh it to the nearest 0.1 mg and record the weight ( $M_d$ ). Repeat this procedure for a total of three determinations for each sample.

2.2 Coating Density. Determine the density of the ink or related coating according to the procedure outlined in ASTM D 1475-60 (Reapproved 1980), (incorporated by reference—see § 60.17).

2.3 Solvent Density. Determine the density of the solvent according to the procedure outlined in ASTM D 1475-60 (reapproved 1980). Make a total of three determinations for each coating. Report the density  $D_v$  as the arithmetic average of the three determinations.

#### 3. Calculations

3.1 Weight Fraction VOC. Calculate the weight fraction volatile organic content  $W_v$ , using the following equation:

$$W_v = \frac{M_v}{M_s}$$

Report the weight arithmetic average.

3.2 Volume Fraction. Calculate the volume fraction  $V_v$  using the following:

$$V_v = \frac{W_v}{D_v}$$

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4.1 Standard Test Methods for Paints, Varnishes, and Related Products. ASTM Designation D 155-80 (Reapproved 1980).

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#### METHOD 25—DETERMINATION OF VOLATILE MATTER CONTENT AND DENSITY OF NONAQUEOUS COATINGS

##### 1. Applicability

1.1 Applicability. This method applies to the measurement of the volatile organic compound (VOC) content and density of nonaqueous coatings (TGNM) which do not interfere with the particulate filter detectable for total carbon.

When carbon vapor are present they can produce a sample. The mass on the concentration vapor. As a guide concentration, express times the water vapor product does not considered insignificant bias is not significant percent CO<sub>2</sub>, and it would be significant detection limit is 20 percent water.

This method is applicable to the Coats, logistics, source testing method.

on VOC

Dishes. Aluminum foil, 18 mm high, with a must be at least three sample.

Syringe. 5 ml.  
Balance. To measure to

um oven capable of temperature of 120±2°C and of 510 ±51 mm Hg for y, a forced draft oven a temperature of 120

ake or mix the sample that all the solids are d. Label and weigh to a weighing dish and

ge without a needle the coating. Weigh the to the nearest 0.1 mg nt ( $M_{w1}$ ). Transfer 1 to to the tared weighing nge and sample to the cord this weight ( $M_{w2}$ ). dish and sample in a absolute pressure of 510 mperature of 120 ±2°C tively, heat the weigh- in a forced draft oven 120 ±2°C for 24 hours.

has cooled, reweigh mg and record the t this procedure for a terminations for each

ty Determine the den- ated coating according lined in ASTM D 1475- 0), (incorporated by ref-

ty. Determine the den- according to the proce- STM D 1475-60 (reap- total of three determin- ing. Report the density c average of the three

on VOC. Calculate the tile organic content W, equation.

$$W_v = \frac{M_{w1} - M_{w2} - M_{w3} - M_{w4}}{M_{w1} - M_{w2}}$$

Eq. 24A-1

Report the weight fraction VOC  $W_v$  as the arithmetic average of the three determinations.

3.2 Volume Fraction VOC. Calculate the volume fraction volatile organic content  $V_v$  using the following equation:

$$V_v = (W_v D_v) / D_s$$

Eq. 24A-2

#### 4. Bibliography

4.1 Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products. ASTM Designation D 1475-60 (Reapproved 1980).

4.2 Teleconversation. Wright, Chuck. Inmont Corporation with Reich, R. A. Radian Corporation. September 25, 1979. Gravure Ink Analysis.

4.3 Teleconversation. Oppenheimer, Robert. Gravure Research Institute with Burt, Rick. Radian Corporation. November 5, 1979. Gravure Ink Analysis.

#### METHOD 25—DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON

##### 1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and, therefore, a particulate filter is required. The minimum detectable for the method is 50 ppm as carbon.

When carbon dioxide ( $CO_2$ ) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of  $CO_2$  and water vapor. As a guideline, multiply the  $CO_2$  concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 percent  $CO_2$  and 10 percent water vapor, but it would be significant for a source near the detection limit having 10 percent  $CO_2$  and 20 percent water vapor.

This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods

more desirable for measuring VOC contents of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semicontinuous nonmethane organics (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semicontinuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane ( $CH_4$ ) will, of course, also be measured. The FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under any of the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentages of the compounds are known or can be determined, and the FID responses to the compounds are known; (4) where a consistent mixture of the compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a heated filter and a chilled condensate trap by means of an evacuated sample tank. After sampling is completed, the TGNMO are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The organic content of the condensate trap fraction is determined by oxidizing the NMO to  $CO_2$  and quantitatively collecting the effluent in an evacuated vessel; then a portion of the  $CO_2$  is re-







## Standard Test Method for Volatile Content of Coatings<sup>1</sup>

This standard is issued under the fixed designation D 2369; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This test method has been approved for use by agencies of the Department of Defense to replace Method 404.1.1 of Federal Test Method Standard No. 1414 and for listing in the DoD Index of Specifications and Standards.*

<sup>1</sup> NOTE—Paragraph 7.3 was editorially corrected and the designation date was changed June 10, 1987.

<sup>2</sup> NOTE—The references to notes and sections in 1.4, 1.2, and 7.3 were editorially corrected in December 1988.

### 1. Scope

1.1 This test method describes a procedure for the determination of the weight percent volatile content of solvent-reducible and water-reducible coatings. Test specimens are heated at  $110 \pm 5^\circ\text{C}$  for 60 min.

1.2 Sixty minutes at  $110 \pm 5^\circ\text{C}$  is a general purpose test method based on the precision obtained with both solvent-reducible and water-reducible coatings (see Section 9). These coatings (single package, heat cured) are commonly applied in factories to automobiles, metal containers, flat (coil) metal and large appliances, and many other metal parts.

NOTE 1—Testing at  $110 \pm 5^\circ\text{C}$  for 20 min was utilized for the establishment of the original test method in 1965. Precision data are not available and may not have been properly generated at the time. The paints tested then were all solvent-reducible. These conditions, 20 min at  $110 \pm 5^\circ\text{C}$ , are no longer satisfactory for the determination of the volatile content of many coatings being tested at the present time. Water-reducible and solvent-reducible coatings were tested in the development of Test Method D 2369 using  $110 \pm 5^\circ\text{C}$  for 60 min and 20 min for which precision data have been generated. See Appendix for precision statements on the 20-min oven residence time.

1.3 This test method does not cover multi-package coatings wherein one or more parts may, at ambient conditions, contain liquid coreactants that are volatile until a chemical reaction has occurred with another component of the multipackage coating.

1.4 This test method may not be applicable to all types of coatings such as printing inks, and other procedures may be substituted with mutual agreement of the producer and user. See Note 3.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. A specific hazard statement is given in 7.3.1.*

### 2. Referenced Documents

#### 2.1 ASTM Standards

D 343 Specification for 2-Ethoxyethyl Acetate (95 % Grade)<sup>2</sup>

D 362 Specification for Industrial Grade Toluene<sup>3</sup>

D 1193 Specification for Reagent Water<sup>4</sup>

E 145 Specification for Gravity Convection and Forced-Ventilation Ovens<sup>5</sup>

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>6</sup>

### 3. Summary of Test Method

3.1 A designated quantity of coating specimen is weighed into an aluminum foil dish containing 3 mL of an appropriate solvent, dispersed, and heated in an oven at  $110 \pm 5^\circ\text{C}$  for 60 min. The percent volatile is calculated from the loss in weight.

### 4. Significance and Use

4.1 This test method is the procedure of choice for determining volatiles in coatings for the purpose of calculating the volatile organic content in coatings under specified test conditions. The inverse value, nonvolatile, is used to determine the weight percent solids content. This information is useful to the paint producer and user and to environmental interests for determining the volatiles emitted by coatings.

### 5. Apparatus

5.1 *Aluminum Foil Dish*, 58 mm in diameter by 18 mm high with a smooth (planar) bottom surface. Precondition the dishes for 30 min in an oven at  $110 \pm 5^\circ\text{C}$  and store in a desiccator prior to use.

5.2 *Forced Draft Oven*, Type IIA or Type IIB as specified in Specification E 145.

5.3 *Syringe*, 5-mL, capable of properly dispensing the coating under test at sufficient rate that the specimen can be dissolved in the solvent (see 7.2).

5.4 *Test Tube*, with new cork stopper.

5.5 *Weighing or Dropping Bottle*.

This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D-1.2 on Chemical Analysis of Paints and Paint Materials.

Current edition approved June 10, 1987. Published August 1987. Originally published as D 2369-65. Last previous edition D 2369-86.

<sup>2</sup> Discontinued, see 1982 Annual Book of ASTM Standards, Part 24.

<sup>3</sup> Annual Book of ASTM Standards, Vol 06.01.

<sup>4</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>5</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>6</sup> Annual Book of ASTM Standards, Vol 15.02.

## b. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II of Specification D 1193.

6.3 *Toluene*, technical grade, Specification D 362.

6.4 *2-Ethoxyethyl Acetate*, technical grade, Specification D 343.

## 7. Procedure

7.1 Mix the sample, preferably on a mechanical shaker or roller, until homogeneous. If air bubbles become entrapped, stir by hand until the air has been removed.

7.2 Using an appropriate weighing container (5.3, 5.4, or 5.5 with the syringe preferred for highest precision), weigh to 0.1 mg, by difference, a specimen of  $0.30 \pm 0.10$  g for coatings believed to have a volatile content less than 40 weight % or a specimen of  $0.50 \pm 0.10$  g for coatings believed to have a volatile content greater than 40 weight %. Into a tared aluminum foil dish (5.5) into which has been added 3  $\pm$  1 mL of suitable solvent (6.2, 6.3, or 6.4). Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one. Similarly prepare a duplicate.

NOTE 2—If the specimen cannot be dispersed in the solvents listed (6.2, 6.3, or 6.4) a compatible solvent may be substituted provided it is no less volatile than 2-ethoxyethyl acetate (6.4).

7.3 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven (5.2) for 60 min at  $110 \pm 5^\circ\text{C}$ .

7.3.1 **Warning**—Provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors

from accumulating to a dangerous level.

7.4 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature and weigh to 0.1 mg.

NOTE 3—If unusual decomposition or degradation of the specimen occurs during heating, the actual time and temperature used to cure the coating in practice may be substituted for the time and temperature specified in this test method, subject to mutual agreement of the producer and user.

## 8. Calculations

8.1 Calculate the percent volatile matter,  $V$ , in the liquid coating as follows:

$$V, \% = 100 - (((W_2 - W_1)/S) \times 100)$$

where:

$W_1$  = weight of dish.

$W_2$  = weight of dish plus specimen after heating, and

$S$  = specimen weight.

8.2 The percent of nonvolatile matter,  $N$ , in the coating may be calculated by difference as follows:

$$N, \% = 100 - \text{volatile matter}$$

## 9. Precision and Bias

9.1 The precision estimated for tests at 60 min at  $110 \pm 5^\circ\text{C}$  are based on an interlaboratory study<sup>8</sup> in which 1 operator in each of 15 laboratories analyzed in duplicate on 2 different days 7 samples of water-based paints and 8 samples of solvent-based paints containing between 35 and 72 % volatile material. The paints were commercially supplied. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.5 % relative at 213 degrees of freedom and the between-laboratories coefficient of variation was 1.7 % relative at 198 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

9.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 1.5 % relative.

9.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 4.7 % relative.

9.2 *Bias*—Bias has not been determined.

<sup>7</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the United States Pharmacopeia.

<sup>8</sup> Supporting data are available from ASTM Headquarters. Request RR D01-1026.

## APPENDIX

### (Nonmandatory Information)

1.1 Oven residence time of 20 min for the paint test oven at  $110 \pm 5^\circ\text{C}$  was the original procedure for this method. For information purposes, the precision statistics for 20-min residence time are:

1.1.1 The precision estimates are based on an interlaboratory study in which 1 operator in each of 15 laboratories analyzed in duplicate on 2 different days 7 samples of water-based paints and 8 samples of solvent-based paints containing from 35 to 72 % volatile material. The paints were commercially supplied. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 1.1 %

relative at 193 degrees of freedom and the between-laboratories coefficient of variation was 2.5 % relative at 178 degrees of freedom. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

(a) *Repeatability*—Two results each the mean of duplicate determinations, obtained by the same operator on different days, should be considered suspect if they differ by more than 2.9 % relative.

(b) *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 7.1 % relative.

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## Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method<sup>1</sup>

This standard is issued under the fixed designation D 4017; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method is applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides, and metal hydroxides. While the evaluation was limited to pigmented products containing amounts of water in the 30 to 70 % range, there is reason to believe that higher and lower concentrations can be determined by this test method.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in Section 7.*

### 2. Referenced Documents

- 2.1 *ASTM Standards*  
D 1193 Specification for Reagent Water<sup>2</sup>  
E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>  
E 203 Test Method for Water Using Karl Fischer Reagent<sup>4</sup>

### 3. Summary of Test Method

3.1 The material is dissolved in pyridine, or another appropriate solvent, and titrated directly with standardized Karl Fischer Reagent, to an electrometric end point. The sluggish reaction with water in pyridine is accelerated with a chemical catalyst, 1-ethylpiperidine.

3.2 Pyridine is used as a solvent to minimize interference problems caused by ketones. It is also used because the more common solvent, methanol, will not dissolve many common resins and because methanol reacts with some resins to produce water.

### 4. Significance and Use

4.1 Control of water content is often important in controlling the performance of paint and paint ingredients, and it is critical in controlling volatile organic compound (VOC) content.

4.2 Paint materials are often insoluble in common Karl Fischer solvents such as methanol. Pyridine has been found to be a nearly universal solvent for these materials; however, the Karl Fischer reaction is too slow in that solvent at room temperature. To speed it up, 1-ethyl-piperidine is added at 5 % as a buffer, or "catalyst."

### 5. Apparatus

5.1 *Karl Fischer Apparatus*, manual or automatic, encompassed by the description in Test Method E 203. Apparatus should be equipped with a 25-mL buret, Class A, or equivalent.

5.2 *Syringe*, 100- $\mu$ L capacity, with needle.

5.3 *Syringes*, 1-mL and 10-mL capacity, without needle, but equipped with caps.

### 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup> Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent grade water conforming to Type II of Specification D 1193.

6.3 *Karl Fischer Reagent*.<sup>5</sup>

6.4 *Pyridine*.

6.5 *1-Ethylpiperidine*.

6.6 *Hydrochloric Acid (HCl) Concentrated*.

### 7. Hazards

7.1 Karl Fischer reagent contains four toxic compounds, namely iodine, sulfur dioxide, pyridine, and methanol or glycol ether. The reagent should be prepared and dispensed in a hood. Care must be exercised to avoid inhalation or skin contact. Following accidental contact or spillage, wash with large quantities of water.

7.2 Pyridine and methanol solvents should be treated with the same care as Karl Fischer reagent.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paints and Related Coatings and Materials and is the direct responsibility of Subcommittee D-10.2 on Chemical Analysis of Paints and Paint Materials.

Current edition approved October 1988. Published December 1988. Originally published as D 4017-78, last previous edition D 4017-73.

<sup>2</sup> Annual Book of ASTM Standards, Vol. 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol. 11.02.

<sup>4</sup> Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rossini, D. Van Nostrand Co., Inc., New York, NY, and the United States Pharmacopoeia.

<sup>5</sup> See Key available from Fischer Scientific Co., or equivalent, as to the suitability for this purpose.

TABLE 1 Specimen Guidelines

Approximate Specimen Weight, g	Approximate Titrant Volume, mL
5	5-10
2-5	10-20
1-2	10-20
0.4-1.0	20-25
0.1-0.4	15-25
0.1	20

1-ethylpyrrolidine is of unknown toxicity and, therefore, should be handled with the same care as the above materials.

## 8. Procedure

### 8.1 Standardization of Karl Fischer Reagent:

8.1.1 Add enough fresh pyridine to cover the electrode tip, plus 1 mL of 1-ethylpyrrolidine catalyst per 20 mL of pyridine. Catalyst performs best at a concentration of about 5 % of the volume present.

8.1.2 Fill the 100- $\mu$ L syringe to about half full with distilled water and weigh to the nearest 0.1 mg.

8.1.3 Pretitrate the pyridine to the end point indicated by the equipment manufacturer, by adding just enough Karl Fischer Reagent I (KFR) to cause the end point to hold for at least 30 s.

8.1.3.1 The use of the catalyst greatly increases the reaction rate between water and Karl Fischer reagent. To obtain reliable results, increase the electrode sensitivity and reduce titration rate to a minimum. Most instruments have controls for these functions. Consult the instructional manual for information on these controls.

8.1.4 Empty the contents of the syringe into the titration vessel. Immediately replace the stopper of the sample port and titrate with KFR to the end point as described in 8.1.3.

8.1.5 Repeat standardization until replicate values of  $F$  agree within 1 %. Determine the mean of at least two such determinations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

### 8.1.6 Calculation:

8.1.6.1 Calculate the KFR titre  $F$  as follows:

$$F = J/P$$

where,

$J$  = water added, g. and

$P$  = KFR used, mL.

The value for  $F$  should be recorded to the four significant digits and should be the mean of at least two determinations. Typical values are in the range of 0.004000 to 0.006000 g/mL.

### 8.2 Analysis of Samples With More Than 0.5 % Water:

8.2.1 The titration vessel should already contain pretitrated pyridine and catalyst, as described in steps 8.1.1 and 8.1.3 in the standardization procedure. Best results are obtained with fresh solvent, that is, contain no previously titrated specimen in the vessel.

8.2.2 With a 1-mL or 10-mL syringe, draw the amount of material indicated in Table 1.

8.2.2.1 Remove the syringe from the specimen, pull the plunger out a little further, wipe the excess material off the

syringe, and place a cap on the syringe tip. Weigh the filled syringe to the nearest 0.1 mg.

8.2.3 Remove the cap, and empty the syringe contents into the pretitrated pyridine vessel. Pull the plunger out and replace the cap. Titrate the specimen with KFR to the end point described in 8.1.3.

8.2.4 Reweigh the emptied syringe, and calculate the specimen weight by difference.

### 8.2.5 Calculation:

8.2.5.1 Calculate the percent water  $L$  as follows:

$$L = (P \times F \times 100)/S$$

### 8.3 Analysis of Materials With Less Than 0.5 % Water

8.3.1 For 0.1 to 0.5 %, follow procedure in 8.2 (1-g specimen), except substitute a 1-mL microburet for the 25-mL buret in the Karl Fischer apparatus.

8.3.2 For less than 0.1 %, use a 1-mL microburet and increase specimen size as much as needed, up to 10 g. It should be possible to measure moisture levels down to 1 ppm (0.0001 %) by this approach.

NOTE—Specimens with less than 0.1 % water may require special handling techniques to prevent pickup of atmospheric moisture. The precision of this test method was determined with specimens containing higher water levels.

## 9. Maintenance

9.1 *Cleanup*—Clean the titration vessel by rinsing with fresh pyridine. Do not use methanol or other solvents.

9.2 *Dryness*—Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace dessicant when indicator color changes through half of the tube.

9.3 *Electrode Performance*—If electrode response is sluggish or otherwise off standard, take the following steps, in turn, to correct the problem. Test the electrode with a titration after each step, to determine if the next step is required.

9.3.1 Wipe the electrode tip with a clean paper towel.

9.3.2 Wash the electrode by dipping in concentrated hydrochloric acid for at least 1 min. Rinse first with distilled water, then with methanol.

9.3.3 Follow manufacturer's instructions on resetting end point meter.

9.3.4 Replace power source. See manual for replacement procedure.

9.3.5 Replace the electrode.

## 10. Precision and Bias

10.1 The precision estimates are based on an inter-laboratory study in which one operator in each of seven different laboratories analyzed in duplicate, on two different days, seven samples of water-based paints of various types containing between 25 to 75 % water. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 1.7 % relative at 98 df, and the between-laboratory coefficient of variation was 5.3 % relative, at 42 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

10.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on

different days should be considered suspect if they differ by more than  $\pm 7\%$  relative.

10.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than  $\pm 15.0\%$  relative.

10.2 *Bias*—Bias has not been determined for this test method.

## 11. Index Terms

11.1 This test method is indexed under the following terms: Karl Fischer reagent method; moisture content; water content (paints, related coatings).

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# Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection Into a Gas Chromatograph<sup>1</sup>

This standard is issued under the fixed designation D 3792; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method is for the determination of the total water content of water-reducible paints. It has been evaluated for latex systems (styrene-butadiene, poly(vinylacetate)-acrylic, acrylic). It has not yet been evaluated for other water-reducible paints but is believed to be applicable. The established working range of this method is from 40 to 55 % water. There is no reason to believe that it will not work outside of this range.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For specific hazard statements, see Section 8.*

## 2. Referenced Documents

- 2.1 *ASTM Standards*
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 1364 Test Method for Water in Volatile Solvents (Fischer Reagent Titration Method)<sup>2</sup>
- E 130 Practice for Determining Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals<sup>3</sup>

## 3. Summary of Test Method

3.1 A suitable aliquot of whole paint is internally standardized with anhydrous 2-propanol, diluted with dimethylformamide, and then injected into a gas chromatographic column containing a porous polymer packing that separates water from other volatile components. The water content is determined from area calculations of the materials producing peaks on the chromatogram.

## 4. Significance and Use

4.1 With the need to calculate volatile organic content (VOC) of water-reducible paints, it is necessary to know the water content. This gas chromatographic test method provides a relatively simple and direct way to determine water content.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.2 on Chemical Analysis of Paints and Paint Materials.

<sup>2</sup> Current edition approved Nov. 28, 1986. Published January 1987. Originally published as D 3792-74; last previous edition D 3792-77.

<sup>3</sup> Annual Book of ASTM Standards, Vol. 11.01.

<sup>4</sup> Copyright © 1986 by ASTM International.

TABLE 1 Instrument Conditions

Detector	thermal conductivity
Temperatures, °C	
Sample inlet	200
Detector	240
Column <sup>a</sup>	
Initial	80
Final	170
Program rate	30/min
Carrier Gas	helium or nitrogen
Flow rate, mL/min	50
Detector current	150 mA
Specimen size	1 $\mu$ L

<sup>a</sup> For isothermal operation set the column temperature at 140°C. After the 2-propanol has cleared the column adjust the temperature to 170°C until DMF clears the column. Reset the temperature to 140°C for subsequent runs.

## 5. Apparatus

5.1 *Gas Chromatograph*—Any gas-liquid chromatographic instrument having a detector may be used. Temperature programming capability is preferable, but isothermal operations may be adequate. See Table 1.

5.2 *Column*—The column should be 4 ft (1.22 m) of  $\frac{1}{8}$ -in. (3.2-mm) outside diameter tubing of stainless steel, or other suitable material, packed with 60/80 mesh (180 to 250  $\mu$ m) porous polymer packing material.<sup>4</sup> A replaceable glass sleeve, glass wool plug, or other suitable material may be placed on the entrance end of the column to retain any nonvolatile materials. This will minimize sludge buildup in the column.

5.3 *Recorder*—A recording potentiometer with a full-scale deflection of 1 to 10 mV, full-scale response time of 2 s or less and sufficient sensitivity and stability to meet the requirements of 5.1.

5.4 *Liquid Charging Devices*—Micro syringes of 10 or 25- $\mu$ L capacity.

## 6. Column Conditioning

6.1 *Procedure*—The packed column is installed in the gas chromatographic unit leaving the exit end disconnected from the detector. This will prevent any contamination of the detector with the column bleed. Set the helium or nitrogen flow rate at 20 to 30 mL/min if a  $\frac{1}{8}$ -in. (3.2-mm) outside diameter column is used. Purge the column 5 or 10 min before heating. Heat the column from room temperature to 200°C at 5°C/min and hold this temperature for at least 12 h (overnight). At the end of this time, heat the column at

<sup>4</sup> Porapak Q<sup>®</sup> a trademark of Waters Assoc., Inc., Milford, MA, has been found satisfactory. Any other porous polymer packing or other column giving equivalents in superior performance may be used. These products are available from most gas chromatograph suppliers and distributors.

5°C min to 250°C (the maximum temperature for this packing) and hold for several hours. Cool the column to room temperature and connect the column detector. Reheat the column to 250°C at 5°C min to observe if there is column bleed. Optimum conditioning of this column may take several cycles of the heating program before a good recorder baseline is achieved.

10.2 Before each calibration and series of determinations (or daily) condition the column at 200°C for 1 h with carrier gas flow.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

7.3 *Carrier Gas*—Helium of 99.995 % or higher purity. High-purity nitrogen may also be used.

7.4 *Dimethylformamide (DMF) (Anhydrous)* gas chromatography, spectrophotometric quality (Note 1).

7.5 *2-Propanol (Anhydrous) (Isopropanol)*—See Note 1.

7.6 *Septum Sample Vials* 10-mL capacity with fluorocarbon-faced septa are preferred.

NOTE 1—Determine the water content of the DMF and 2-propanol by Karl Fischer titration in accordance with Test Method D 1364. Dry the 2-propanol if water is found in it or replace with anhydrous grade.

## 8. Hazards

8.1 *Dimethylformamide* is harmful if inhaled or absorbed through skin. It is suspected to be embryotoxic. Use only with adequate ventilation. Avoid contact with skin, eyes, and clothing. Refer to supplier's Material Safety Data Sheet.

## 9. Preparation of Apparatus

9.1 Install the column in the chromatograph and establish the operating conditions required to give the desired separation (see Table 1). Allow sufficient time for the instrument to reach equilibrium as indicated by a stable base line. Control the detector temperature so that it is constant to within 1°C without thermostat cycling which causes an uneven baseline. Adjust the carrier-gas flow to a constant value.

## 10. Calibration

10.1 Using the information in Table 1 (as a guide), select the conditions of temperature and carrier gas flow that give the necessary resolution of the components.

10.2 *Determination of Relative Response Factors*—Anhydrous 2-propanol is used as an internal standard. The

response factor to water relative to the standard is determined by means of the following procedure. See Fig. 1 for a typical chromatogram. It is good practice to determine the relative retention time daily or with each series of determinations.

10.2.1 Weigh about 0.2 g of water and 0.2 g of 2-propanol to 0.1 mg into a septum sample vial. If it has been determined that a correction for the water content is necessary, weigh 2 mL of dimethylformamide (DMF) into the vial. If the DMF is anhydrous, simply add 2 mL of it as weighing is not necessary.

10.2.2 Inject a 1-μL aliquot of the above solution into the column and record the chromatogram. The retention order and approximate retention times after the air peak are (1) water, about 0.7 min; (2) 2-propanol, about 2.8 min; and (3) DMF, about 7 min.

10.2.3 The preferred procedure to obtain the water content of the DMF is the Karl Fischer titration (Note 1). If this has been determined, calculate the response factor for water by means of the following equation:

$$R = \frac{W_2 A_{H_2O}}{(W_{H_2O} + P W_2) A_2}$$

where:

$R$  = response factor.

$W_2$  = weight of 2-propanol.

$W_{H_2O}$  = weight of water added.

$W_2$  = weight of dimethylformamide.

$A_{H_2O}$  = area of water peak.

$A_2$  = area of 2-propanol peak, and

$P$  = weight % water in DMF

100

10.2.4 If Karl Fischer titration is not available, the following procedure may be used to obtain a reasonable

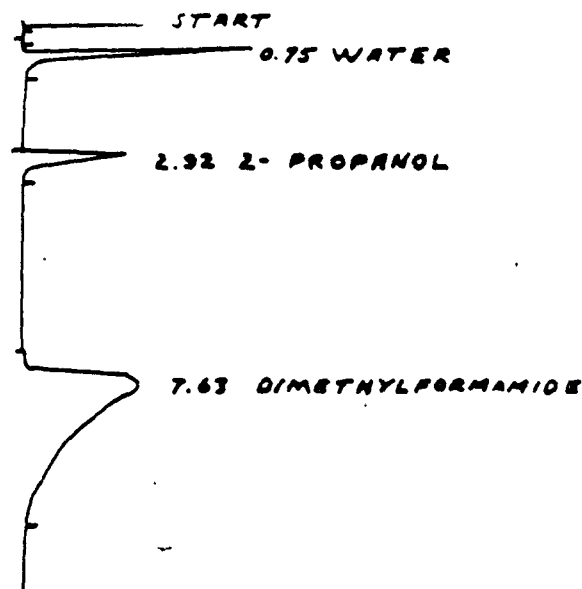


FIG. 1 Typical Chromatogram

<sup>5</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., New York, NY, and the "United States Pharmacopeia."

estimate of the response factor:

10.2.4.1 Inject the same size aliquot of DMF and 2-propanol mixture, but without added water, as a blank. Note the area of the water peak in the blank.

10.2.4.2 The response factor for water is calculated by means of the following equation:

$$R = \frac{W(4_{H_2O} - B)}{4_{H_2O}}$$

where:

- $R$  = response factor.
- $W$  = weight of 2-propanol.
- $W_{H_2O}$  = weight of the water.
- $A_i$  = area of 2-propanol peak.
- $4_{H_2O}$  = area of the water peak, and
- $B$  = area of the water peak in the blank.

## 11. Procedure

11.1 Weigh to 0.1 mg, 0.6 g of water-reducible paint (see Note 2) and 0.2 g of 2-propanol into a septum vial. Add 2-mL of DMF into the vial. Seal the vial. Prepare a blank containing the 2-propanol and DMF but no paint.

NOTE 2—Check each paint system to be analyzed for interfering peaks. Coalescing agents do not interfere with this determination.

11.2 Shake the vials on a wrist action shaker or other suitable device for 15 min. To facilitate settling of solids allow the vials to stand for 5 min just prior to injection into the chromatograph. Low-speed centrifugation may also be used.

11.3 Inject a 1- $\mu$ L sample of the supernatant from the prepared solutions into the chromatographic column. Record the chromatograms using the conditions described in Table 1.

## 12. Calculations

12.1 Measure the area of the water peak and the 2-propanol internal standard peak and multiply each area by the appropriate attenuation factor to express the peak areas on a common basis. Use of an electronic integrator is recommended to obtain the best accuracy and precision. However, triangulation, planimeter, paper cut out, or ball and disk integrator may be used.

12.2 Calculate the water concentration in the paint by means of the following equation:

$$H_2O, \% = \frac{4_{H_2O} \times W \times 100}{4 \times W \times R}$$

where:

- $4_{H_2O}$  = area of water peak.
- $4_i$  = area of 2-propanol peak.

$W$  = weight of 2-propanol added.

$W_p$  = weight of paint, and

$R$  = response factor determined in 10.2.

### 12.3 Correction for Water Content of Solvent

12.3.1 If the blank indicates the presence of a detectable peak for water in the dimethylformamide used as solvent, make a correction in the calculation.

12.3.2 The water content of the dimethylformamide determined by either chromatography (10.2.4) or, preferably, Karl Fischer titration (10.2.3) is used to make the correction. Calculate the water content due to the solvent by using the following equation:

$$H_2O(S), \% = \frac{(W_s \times P)100}{W_p}$$

where:

$W_s$  = weight of dimethylformamide.

$W_p$  = weight of paint, and

$P$  = weight % water in DMF  
100

12.3.3 The water content of the paint in this case is the difference between the total percent determined in 12.2 and the correction for the solvent water content as determined in 12.3.2.

## 13. Precision and Bias<sup>6</sup>

13.1 The precision estimates are based on an inter-laboratory study in which nine different laboratories analyzed in duplicate on two days four samples of water-reducible paints containing from 40 to 55 %  $H_2O$  (theoretical). The results obtained were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 1.0 % relative at 34 degrees of freedom and the between-laboratories coefficient of variation 2.6 % relative at 30 degrees of freedom. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

13.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 2.9 % relative.

13.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 7.5 % relative.

13.2 *Bias*—Bias has not been determined.

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR D11-1022.

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## APPENDIX ii



### Soybean Oil Volatility Test Results

Test Date: December 5, 1990  
Analysis: Gravimetric portion of Method 24  
Equipment: Mettler PM 100 Balance, Fisher Forced Draft Oven  
Temperature: 234 °F, 112.2 °C  
Analyst: Rima Dishakjian  
Prepared for: Madeleine Strum, CPB, MD-13

#### Food Club Soybean Oil

Sample Number	Percent Volatile
1	0%
2	0.1%
3	0.1%

#### Wesson Soybean Oil

Sample Number	Percent Volatile
1	0%
2	-0.1%
3	-0.3%

It would be safe to assume that the soybean oils tested are not volatile according to the Method 24 definition. Any positive or negative percent volatile value is probably due to variability in the balance used to weigh the samples and is not real.





## APPENDIX iii

# Method 24A Analysis of Vegetable Oils

Test Date: 2/12/91 to 2/13/91  
 Equipment: Mettler PM 100 Balance, Fisher Isotemp Forced Draft Oven  
 Temperature: 248 F, 120 C  
 Analyst: Rima Dishakjian  
 Prepared for: Madeleine Strum, CPB, MD-13

TYPE OF OIL	CODE	EMPTY PAN (g)	PAN + OIL (g)	WEIGHT OF OIL (g)	WEIGHT AFTER	WEIGHT CHANGE	AVERAGE CHANGE
R-B SOYBEAN OIL	1	1.438	3.452	2.014	3.477	1.24%	1.25%
	2	1.439	3.766	2.327	3.799	1.42%	
	3	1.434	3.443	2.009	3.465	1.10%	
R-B-D COTTONSEED OIL	4	1.438	3.467	2.029	3.477	0.49%	0.63%
	5	1.438	3.47	2.032	3.483	0.64%	
	6	1.436	3.45	2.014	3.465	0.74%	
R-B-D SUNFLOWER OIL	7	1.441	3.545	2.104	3.555	0.48%	0.62%
	8	1.422	3.544	2.122	3.558	0.66%	
	9	1.433	3.47	2.037	3.485	0.74%	
R-B-D CANOLA OIL	10	1.418	3.459	2.041	3.475	0.78%	0.87%
	11	1.43	3.45	2.02	3.468	0.89%	
	12	1.432	3.464	2.032	3.483	0.94%	
R-B LINSEED OIL Note: solidified	13	1.313	3.344	2.031	3.389	2.22%	2.30%
	14	1.31	3.366	2.056	3.413	2.29%	
	15	1.31	3.311	2.001	3.359	2.40%	
CRUDE LINSEED OIL Note: solidified	16	1.308	3.312	2.004	3.356	2.20%	2.14%
	17	1.434	3.492	2.058	3.535	2.09%	
	18	1.308	3.416	2.108	3.461	2.13%	

# Method 24A Analysis of Vegetable Oils

Test Date: 2/12/91 to 2/13/91  
 Equipment: Mettler PM 100 Balance, Fisher Isotemp Forced Draft Oven  
 Temperature: 248 F, 120 C  
 Analyst: Rima Dishakjian  
 Prepared for: Madeleine Strum, CPB, MD-13

TYPE OF OIL	CODE	EMPTY		PAN +		WEIGHT OF OIL (g)	WEIGHT AFTER	WEIGHT AVERAGE	
		PAN (g)	PAN (g)	OIL (g)	OIL (g)			CHANGE	CHANGE
VERNONIA OIL Note: dried	19	1.437		2.541	1.104	2.494	-4.26%	-3.54%	
	20	1.435		2.571	1.136	2.526	-3.96%		
	21	1.307		3.518	2.211	3.465	-2.40%		
CRUDE SOYBEAN OIL	22	1.311		3.356	2.045	3.367	0.54%	0.51%	
	23	1.438		3.438	2	3.448	0.50%		
	24	1.425		3.448	2.023	3.458	0.49%		
CRUDE COTTONSEED OIL	25	1.304		3.371	2.067	3.371	0.00%	0.01%	
	26	1.432		3.472	2.04	3.47	-0.10%		
	27	1.431		3.753	2.322	3.756	0.13%		
TUNG OIL Note: Crystallized	28	1.437		3.531	2.094	3.602	3.39%	3.56%	
	29	1.435		3.463	2.028	3.537	3.65%		
	30	1.434		3.569	2.135	3.647	3.65%		
R-B-D SOYBEAN OIL	31	1.439		3.467	2.028	3.48	0.64%	0.66%	
	32	1.418		3.523	2.105	3.537	0.67%		
	33	1.434		3.47	2.036	3.484	0.69%		

R - refined  
 B - bleached  
 D - deodorized



## APPENDIX iv



## FRYING OPERATIONS REFERENCES

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TECHNICAL REPORT DATA		
(Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-450/3-91-011	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE The Impact of Declaring Soybean Oil Exempt from VOC Regulations on the Coatings Program	5. REPORT DATE April 1991	6. PERFORMING ORGANIZATION CODE
	8. PERFORMING ORGANIZATION REPORT NO.	
7. AUTHOR(S) Madeleine L. Strum, EPA Candace Blackley, Radian	10. PROGRAM ELEMENT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Emission Standards Division Office of Air Quality Planning and Standards U.S. Environmental Protection Agency (MD-13) Research Triangle Park, NC 27711	11. CONTRACT/GRANT NO. 68-02-4378	
	13. TYPE OF REPORT AND PERIOD COVERED Final	
12. SPONSORING AGENCY NAME AND ADDRESS Emission Standards Division Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE	
	15. SUPPLEMENTARY NOTES	
16. ABSTRACT  This document presents the findings of a study to evaluate the impact of declaring soybean and other vegetable seed oils exempt from VOC regulation on the coatings program. The physical and chemical characteristics of 10 vegetable seed oils are tabulated and their uses are discussed. Tests conducted with EPA reference Methods 24 and 24a showed no weight loss, indicating that the oils contain no VOC. However, the study discloses that VOC's are emitted during the autoxidation reaction which occurs when these oils are in contact with atmospheric oxygen.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Volatile Organic Compounds Air Pollution Vegetable Oils Method 24		
18. DISTRIBUTION STATEMENT Release Unlimited	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 65
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

