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PETROLEUM PRODUCTS HANDBOOK

VIRGIL B. GUTHRIE, Editor

Formerly Editor of Petroleum Processing and Managing Editor of National Petroleum News

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Section 11

MISCELLANEOUS LIGHT OILS

PART 1. KEROSINE (ILLUMINATING OIL)

By VIRGIL B. GUTHRIE

Editor

Kerosine—the petroleum industry spells it with an *i*—is the oldest petroleum product which U.S. refiners make and sell today. First known as coal oil, it was distilled from oil from seepages a few years before the drilling in of Pennsylvania's Drake well in 1859 revolutionized the means of recovery of crude oil from the ground and launched a petroleum industry.

Writing from New York in 1860, Abraham Gesner, a consulting chemist, stated: "During the past year numerous springs of petroleum have been opened in some of the Western States and oils are produced from them which are not inferior to those obtained from the most approved varieties of coal.

"The petroleum oils differ from those produced from coal. They require greater heat in their distillation and their vapors are extremely inflammable. These petroleum oils usually commence to boil at 160°F but sometimes at a still lower degree of heat."

This authority listed 56 companies manufacturing coal oil in the United States at that time and stated there were also 15 establishments where petroleum only was worked.[1,*]

Kerosine remained the principal volume product of the refiners in this country for 50 years, both in domestic and in foreign trade. It was used as an illuminating oil and to some extent, particularly in the United States, for cooking and limited space heating. The distribution of the product was so extensive that, when automobiles began to be used, inventors turned their hand to the effort to develop a kerosine carburetor for the early automobile engines. It was even feared by some that the supplies of straight-run gasoline the refiners were then making as a byproduct of kerosine manufacture would not be sufficient to supply the automobiles of the future. The development of the petroleum cracking process just prior to World War I ensured ample supplies of gasoline for motor fuel.

In the succeeding years, other uses for kerosine have developed, and the widening availability over the country of natural and manufactured gas and electricity has cut into the market for this product for domestic lighting and cooking. The advent of oil heating for houses, churches, schools, and buildings of this type has created a

* Superior numbers indicate references on page 11-7.

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demand for kerosine as range oil, meeting the requirements of No. 1 distillate fuel oil. This is the present largest-volume market. (For a discussion of this use see Sec. 7, Distillate Heating Oils.) It also serves as fuel for heavy tractors and marine engines, as a solvent, as a pesticide, and in many specific industrial uses. It is also a component of jet fuels. Since 1952, the production of kerosine at refineries for this last-named use has been reported separately. (For a discussion of this use see Sec. 5, Aircraft Gas Turbine Fuels.)

Thus, although sales of kerosine as an illuminating oil have decreased steadily during the past 50 years, other uses have developed which maintain kerosine as a volume product of refiners in this country. The rate of increase in its demand, however, has been far less than for most petroleum products. In 1918, for example, the refinery output of kerosine was 43,461,000 barrels—about half the production of gasoline. By 1957 the refinery production of kerosine had grown to 108,929,000 bbl. Gasoline production had grown from 85,007,000 bbl in 1918 to 1,438,408,000 bbl in 1957. Refinery output of kerosine, exclusive of that going into jet fuels, by 1957 was about one-thirteenth of the volume of gasoline U.S. refiners were making.

As shown in Table 11-1, total sales of kerosine in the United States in 1957 were 102,378,000 bbl. Of this 75,760,000 bbl were classified as range oils, 2,422,000 bbl as tractor fuel, and 24,306,000 bbl for all other uses. This classification includes the sales of this product as an illuminating oil. Here, despite the wide availability today of natural gas and electricity, kerosine serves many essential uses: in lighthouse beacons, miners' lamps, railroad-signal systems, and so on. For these uses, special grades of kerosine are generally required.

Table 11-1. U.S. Kerosine Production and Demand, 1948 to 1957
(1,000 bbl)

Year	Sales in the United States					Exports	Total demand
	Refinery production	Range oil	Tractor fuel	Other uses	Total U.S. sales		
1957	108,929	75,760	2,422	24,306	102,378	5,787	107,665
1956	123,480	86,050	2,465	28,519	116,834	3,297	120,131
1955	119,087	84,351	2,804	28,745	115,880	3,395	119,185
1954	122,305	85,224	3,125	29,568	117,915	4,852	122,767
1953	123,200	82,671	3,226	28,509	114,397	7,265	121,662
1952*	126,767	86,866	3,569	32,194	122,629	7,963	130,592
1951	135,742	86,623	4,025	32,586	123,228	6,843	130,071
1950	118,512	79,869	4,138	34,285	118,284	2,078	120,362
1949	102,152	66,244	4,840	31,527	102,661	2,535	105,196
1948	121,914	70,629	6,176	35,681	112,487	3,495	115,982

Source: Mineral Oil Surveys, *U.S. Bur. Mines.*
* Starting with 1952, the production of kerosine used as a component of jet fuels is listed separately.

Kerosine is defined as a refined petroleum distillate having a flash point not below 73°F (23°C) and suitable for use as an illuminant when burned in a wick lamp.[1] The specifications of the United States government and many states provide a minimum flash point requirement of 115°F. In some states it is higher.

The petroleum-base oil from which it is manufactured is the second cut, or "water-white" fraction, from the distillation of crude petroleum. This distillate varies in color, sulfur content, burning quality, and flash point according to the nature of the crude petroleum from which it is processed. Its gravity is generally within the range of 40 to 46°API, and its burning point within the range of 150 to 175°F. The burning point is the lowest temperature at which a volatile oil in an open vessel will burn continuously when ignited by a flame held close to its surface. The burning point, or fire point, is an important indication of the degree of safety with which the kerosine product made from refinery distillate can be handled and used. Despite variations in the distillate arising from the nature of the crude petroleum from which it is distilled, modern treating methods in the refinery provide for holding the finished kerosine product to the desired specifications.

The nature of kerosine and its wide uses as an illuminating oil require not only that the product have the proper burning qualities, as determined by scientific test methods, but also that it be safe to transport, handle, and use in lamps and burners. Specifications to ensure both these requirements have been in effect for many years in many states and municipalities. The physical and chemical properties of kerosine to meet the Federal government specifications are given in Table 11-2. The ASTM has no specification for kerosine as an illuminant, but its standards for No. 1 distillate fuel oil, also known as range oil, are similar in many respects to the specifications of other agencies for kerosine.[2]

Table 11-2. Physical and Chemical Requirements for Kerosine and Designated Tests in U.S. Specifications

Property	Requirement	ASTM test method
Flash point, °F, min.	115	D 56
End point, °F, max.	572	D 86
Sulfur, %, max.	0.15	D 90
Color, Saybolt chrom. no darker than	+21	D 156
Color, Saybolt chrom. (after heating 16 hr) no darker than	+16	D 156
Burning test, hr, min.	16	D 187
Cloud point, °F	5	D 97

Some states still inspect kerosine for safety purposes, and flash point and other properties are legally prescribed and must be met by the product, regardless of the use to which the kerosine is put. Distillation range, particularly final boiling point and sulfur content, is an important property of kerosine when used as an illuminant, and it is included in some state requirements. Color is sometimes included, for even though it has little significance in performance, it is the first property to which the consumer pays attention. Color also can indicate long storage of the product. The tests which determine the properties of kerosine are included in the ASTM standard test methods. They are reviewed briefly in the following paragraphs. The property requirements in the state specifications are summarized in Table 11-3.

THE ESSENTIAL PROPERTIES OF KEROSINE

Flash Point. The lowest temperature at which vapors arising from the oil sample will ignite momentarily, or flash, on application of a flame under specified test conditions is an important property of kerosine for safety as well as for performance requirements. Flash point of kerosine is taken with the Tag closed-cup tester, ASTM D 56, and the minimum allowable flash temperature is generally placed above the prevailing ambient temperature.

The inclusion of a flash-point requirement in kerosine specifications today goes back to the time when this oil was the principal product made at the refinery and gasoline was a byproduct. The natural tendency then was to include, in what was sold as kerosine, a proportion of the more volatile fractions that today go into gasoline. Explosions and fires resulting in the early days from the transportation and use of kerosine in lamps, cook stoves, and heaters led to the adoption of means to reduce this danger. This was done by setting up a flash-point requirement, which is, in effect,

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Table 11-3. Properties for Kerosine Specified in State Inspection Laws

State	Flash point °F, min	End point °F, max	Sulfur %, max	Color, Saybolt, no darker than	Burning test hr, min	Cloud point, °F
Alabama	115	572	0.125	+21		
Arkansas	140*					
Colorado	115	625	0.20	+16	16	5
Florida	115	572	0.13	+16		
Georgia	115	572	0.125	+16	16	
Idaho	115	626	0.13	+16	16	5
Illinois	115	550	.....	+16		
Indiana	120	550	.....	+16		
Kansas	115					
Louisiana	115	625	0.125	+16	16	5
Minnesota	120	600				
Mississippi	115	575	0.25	+16	16	5
Montana	110					
Nebraska	115	625	0.125	+16	16	5
New Hampshire	110					
New Mexico	115	550	0.30	....	16	
New York	100					
North Carolina	115	572	0.13			
North Dakota	115	572	0.13	+16	16	5
Oklahoma	115					
Pennsylvania	110*					
South Carolina	110†	570				
South Dakota	115	572	0.13	+16		
Tennessee	112	600	0.13	+16	16	5
Wisconsin	110	572	.....	+16		
Wyoming	115	625	0.125	+16	16	5

* Fire point.
† Elliot closed-cup method.

the lower limit of inflammability of the product. In the government specifications and in those in many states, the minimum flash point stipulated is 115°F (in a few instances it is a few degrees lower).

Of the significance of flash point in determining the volatility of this petroleum product, an ASTM bulletin[4] states:

> The flash points of kerosine and naphtha are important in determining the fire hazard. For this reason, there are flash point requirements in force for these products in many different municipalities, states and countries. The fact that there are variations, sometimes wide ones, in these requirements merely reflects the needs in the various areas to recognize differences in the conditions under which the products may be handled. These needs take into effect the familiarity, or lack of familiarity, of the users with the hazards involved. The imposition of a minimum flash requirement for safety is, therefore, a recognition of the fact that kerosine and naphtha can be handled with reasonable safety in open vessels and cans by people who are not thoroughly familiar with fire and explosion hazards.

The lengths to which some states and municipalities have gone in legislation and regulations to protect individuals from the fire hazards associated with flammable liquids are illustrated by the General Business Law of New York State. This law was passed in 1882 and is still in effect, the last amendment apparently being in 1929. This statute prescribes a minimum flash point of 100°F for illuminating oils sold within the state but goes on to set up further restrictions as follows:

> No such oil or fluid which will ignite at a temperature below 295°F as determined by the standard method of test for flash and fire points, by means of open cup, of the ASTM, shall be burned or carried as freight in any passenger or baggage car or passenger boat moved by steam or electric power in this State, or in any stage or street car, however propelled, except that coal oil, petroleum and its products may be carried, when securely packed in barrels or metallic packages, in passenger boats when there are no other means of public transportation.
>
> Naphtha and other illuminating products of petroleum which will not stand the flash point required by this section, may be used for illuminating or heating purposes only in the following cases:
>
> 1. In street lamps and open receptacles apart from any building, factory, or inhabited house in which the vapor is burned.
>
> 2. In dwellings, factories or other places of business when vaporized in secure tanks or metallic generators made for that purpose in which the vapor so generated is used for lighting or heating.
>
> For use in the manufacture of illuminating gas in gas manufactories situated apart from dwellings and other buildings.

Fire Point. In a few instances the fire point of an illuminating oil is used to determine the fire hazards associated with its handling and use. This property is determined by ASTM D 92, Method of Test for Flash and Fire Points by the Cleveland Open Cup. To determine fire point, the test for flash point by this procedure is continued until the application of the test flame causes the oil to ignite and burn at least 5 sec. The government specifications contain no fire-point requirement. A fire point of 140°F is standard in Arkansas and of 110°F in Pennsylvania.

Distillation Range. The boiling range of kerosine is of less importance than for gasoline, but it can be taken as an indication of the viscosity of the product. The Federal government and state specifications for distillation temperatures are generally limited to the end, or final, boiling point. In the former standards, 572°F is the maximum final boiling point, as determined by ASTM D 86. While many states have the same end-point limit, there is more variation here than among other property requirements of the product, namely, from 550°F in Indiana and New Mexico to 625°F final boiling point in a few states.

Viscosity. Although there is no viscosity requirement for kerosine in the Federal and state specifications, the ASTM[4] states on this subject:

> For illuminating oils, the value of a viscosity test is mainly to determine whether they may be of abnormally high viscosity, which may not allow them to flow properly through the wicks of lamps and burners; or may be of very low viscosity, which may cause unsteady flames. The performance of burning oils is influenced less by viscosity than by the tendency to incrust the wick. An actual burning test is the best way to determine the quality of an illuminating oil, as it indicates the combined effect of all the important properties.

Burning Test. The ability of a kerosine to burn steadily and cleanly over an extended period is determined by the burning test. The standard test (ASTM D 187) provides that the kerosine be burned in a wick lamp for a specified period (generally 24 hr) in a room free from drafts. The average rate of burning, the change in the shape of the flame, the density and color of the chimney deposit, and the condition of the wick are the factors by which the burning quality of the oil is determined. More severe test methods are used for determining the quality of the special grade of kerosine used in railway semaphore signal lamps (D 219) and for the special illuminating oils known in the trade as mineral seal oil, 300 oil, or mineral colza oil used in railway coach and caboose lamps (D 239).

The burning qualities of kerosine, according to government specifications, are determined after a minimum of 16 hr continuous burning under the test conditions prescribed in D 187. At the end of the test the chimney must be clean or only slightly clouded, the wick must have no appreciable hard incrustations, and the flame must not be smoky and must be practically as large at the end of the test as when the final adjustment of the wick was made. Most of the state specifications also require a 16-hr burning test. Of the significance of the burning test for illuminating oils, the ASTM report[4] states:

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Burning tests are essentially performance tests and are a direct method for determining the quality of the oils for the specific purpose for which they are intended. However, it is not possible to make tests in all kinds of commercial equipment, or under all the combinations of such factors as location, time, temperature, humidity, air currents and cleanliness. These difficulties are overcome, at least partially, by selecting equipment for the burning test that is known to be severe on the oil and by extending the test beyond the average time interval between cleanings of the lamp in its usual service.

None of the standard burning test methods gives results that can be evaluated adequately in numerical terms. They do prescribe efficient procedures for comparing the burning qualities of different samples or grades of oil, particularly as regards behavior details. It is relatively easy to tell a very good oil from a very bad oil but this question rarely occurs. The usual need is for information as to whether the oil is slightly better or worse than the standard. To supply such information, it is necessary to rely on the observations of a skilled operator and to interpret these observations in terms of the service requirements of the products.

The most important features in a burning test are the shape and size of the flame. Occasionally, an oil has a viscosity so low that the flame increases, or so high that it decreases, during the burning period. However, changes in flame size or shape are generally caused by changes in the portion of the wick adjacent to the flame. An incrustation always forms on the wick. It is not objectionable unless it affects the flame. Some wick crusts are "bushy" and increase flame size; others tend to enclose the surface of the wick and cause flame shrinkage. The worst type of deposit, however, is an irregular one, sometimes localized as mushroom formations. This type produces a distorted flame and usually causes smoking, which is quite objectionable to the user.

The condition of the chimney at the end of the burning test is important. Illuminating oils should not cloud or smoke the chimney. A black sooty deposit is obviously objectionable, but the operator must always assure himself that it is not caused by drafts or improper testing techniques. A heavy whitish deposit nearly always forms when a new chimney is put into service.

If burning-test equipment is not available—the same authority points out—or if there is not enough time to make the extended burning tests, which range in burning time from 20 hr to 6 days, a reasonably reliable idea of the quality of an illuminating oil for a particular purpose can be obtained from a judicious consideration of its gravity, flash point, viscosity, pour point, sulfur content, color, distillation range, and cloud point.

Sulfur Limitation. The significance of the total sulfur content of an illuminating oil varies greatly with the type of oil and the use to which it is to be put. In general, sulfur content is important only when the oil is to be burned under conditions where the sulfur oxides that may be produced during combustion must be limited, as in lamps and heating equipment not connected by an outside flue to the outdoor atmosphere. In household or industrial furnaces, the sulfur content of the oil is usually significant only in those installations where economizers or air preheaters of high efficiency permit condensation of the moisture from the flue gases on cool metal surfaces, with resultant corrosion.

The government specifications for kerosine provide a maximum of 0.13 per cent sulfur, as determined by ASTM D 90. Requirements in the state specifications vary from 0.125 per cent maximum to at least one instance (New Mexico) of a maximum limitation of 0.3 per cent.

Color. The color of kerosine has little significance in indicating the performance quality of the product, but it is included in most specifications, since it is the first property to come to the attention of the user. A product darker than the standard may have resulted from aging or contamination, and it is desirable to market a kerosine of uniform color. Color for kerosine, as for many petroleum products except lubricating oils, is determined by the Saybolt chromometer method (ASTM D 156). Color, by this method, is related to the depth of a column of a sample of the oil, the color of which is compared with specified glass standards. The range of the numbers is from −16 to +30. The larger the number, the lighter the color. The government specifications provide that the color of the product sample shall not be greater than +21 and not darker than +16 after heating the sample for 16 hr. Most of the state standards provide that the color of the sample, before heating, shall be no darker than +16. A product which is off color by test from the color standard by four numbers is considered unsatisfactory by some agencies.

Cloud Point. This test of an illuminating oil or a heating oil of low viscosity to be used in wick service is an indication of the temperature at which the wick may become coated with wax particles, thus lowering the burning qualities of the oil. The cloud point is taken by ASTM D 97, in which a sample of the oil, free from moisture, is poured into a test jar and cooled in successive stages. When inspection first shows a distinct haze or cloudiness at the bottom of the jar, the temperature is recorded as the cloud point. The government standards for kerosine and the state specifications usually provide a 5°F cloud point.

In a few states a floc test is included in their kerosine specifications. This is a qualitative test to determine the presence of small flakelike bits of substances rendered insoluble by heat. In the main, however, the state requirements follow the government standards as shown in Table 11-2, ensuring a quality of kerosine for illuminating and other uses which both gives good performance values and provides for the safety of the product under all normal procedures.

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1. *A Practical Treatise on Coal, Petroleum and Other Distilled Oils*, Abraham Gesner, New York, 1860.
2. *Glossary of Terms Used in Petroleum Refining*, American Petroleum Institute, 1953.
3. *ASTM Standards for Petroleum Products and Lubricants*, American Society for Testing Materials, 1956.
4. *Significance of ASTM Tests for Petroleum Products*, American Society for Testing Materials, 1955.

GUIDE TO CURRENT AND PRIMARY REFERENCE DATA

KEROSINE (ILLUMINATING) OIL

For titles of reports indexed below see Reference Data Directory, Part 1 of Sec. 16.

Sampling and Measurement. API-22, ASTM-3, ASTM-4.
Specifications and Properties. ASTM-1, ASTM-5, MPSA-1, WPRA-1.
Testing Methods. ASTM-1, GPO-6.
Storage, Handling, and Transportation. API-25, API-34, BE-1, CG-2, NFPA-2, NFPA-4.
Supply-Demand and Utilization. API-8, API-26, BM-9, BM-16, BM-8.
Sources of Supply. BM-8, MHPC-3, OGJ-1.
Prices and Price Trends. BM-7, IPAA-1, MHPC-1, OGJ-3.
Special Taxes, Inspection. API-33, WPRA-1.

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PART 2. INDUSTRIAL NAPHTHAS

By MARTIN B. CHITTICK

Consulting Engineer
Winter Park, Fla.

The utilization of hydrocarbons derived from petroleum as solvents and thinners in modern industry has had a fantastic growth over the past few years, to such a degree that, in the over-all volume employed, these hydrocarbons probably rank second to the universal solvent, water.

Historically, these naphthas, or petroleum solvents, have been available since the first barrel of crude oil was run through a still. It is this modest beginning that dates the oldest and best known naphtha, *mineral spirits*. However, this early naphtha was made to no rigid specifications, as we know and understand such standards today. It was a product of uncertain properties and left much to be desired in the way of uniformity. Prior to the advent of the automobile, the production of this early naphtha far exceeded the demand and at times posed a serious disposal problem to the petroleum-refining industry. Efforts made in this period to develop a market for naphthas as a replacement for turpentine in the paint and varnish industry met only limited success and even considerable opposition.

In our modern economy this situation is not difficult to understand. Pioneer refiners in the petroleum industry had little or no scientific knowledge that would permit them to offer sound advice on product application to the consuming industries. Furthermore, the paint and varnish industry at this time had not departed from its status as an art. In the coating industry, as well as in many other industries, the acceptance of industrial naphthas derived from petroleum was based upon trial-and-error applications.

That the production and use of these industrial naphthas have had such a phenomenal growth within recent years can be attributed almost entirely to research and development. Within the petroleum industry a basic change has taken place in that it has adopted a scientific approach to its many problems. In fact, it has become a major chemical industry within itself. From an industry based on essentially a simple separation of petroleum fractions by distillation, the modern refinery has become an integrated operation of physical and chemical processes. Concurrently, progress has been substantial in the development of laboratory procedures of testing for the accurate determination of the component compounds that go to make up crude petroleum and natural gas, as well as the refined products derived from them. From the laboratory has come technical knowledge that has permitted better physical separation of these component compounds. Research has produced chemical processes capable of changing the naturally occurring compounds, through thermal and catalytic cracking, reforming, alkylation, and similar processes, into the type of compounds demanded by a growing industrial economy.

The modern petroleum refinery is an extremely flexible institution, capable of producing hydrocarbons of a high degree of purity through the entire gamut of conventional petroleum products. Specifically, this has made possible the manufacture of industrial solvents with almost any practical quality or property required by modern industry, particularly as to boiling range and solvency.

Along with these technical developments in the petroleum industry have come scientific achievements in the solvent-consuming industries. As a specific example, the development of the entire synthetic-resin industry and the wide use of these resins would have been seriously curtailed had not the industrial naphthas essential to their operations been widely available. All these developments in the consuming industries and by the oil companies, therefore, have complemented one another. The economics of modern industry have also been a contributing factor, for the industrial naphthas are consistently lower in cost than the organic solvents, such as the alcohols, esters, and ketones. This fact, together with the ready availability of the industrial naphthas, has been a major contributing factor to the rapid growth in the use of petroleum solvents.

Prior to World War II, the aromatic naphthas were produced by the fractional distillation of coal tar and coal-tar residues. These included benzene, toluene, xylene, and high-flash aromatic naphthas. With technical developments and the adoption of new processes in petroleum refining, a high proportion of these aromatics, plus other types of aromatics not previously available, are now produced by the petroleum industry. In general, however, the aromatics from either source are essentially the same in all respects, with the possible exception of a few specific organic chemical materials originally based on coal tar. The conventional qualities of products from the two sources, such as boiling range, solvency, and so on, are the same. We are concerned here with the industrial naphthas produced from petroleum sources. In fact, the new processes now used in petroleum refining are producing intermediate- and high-boiling-point types of naphthas that are not available from coal-tar sources.

Major uses of industrial naphthas are as solvents, thinners, and diluents. Through the years some confusion has developed over these terms. In some literature, for example, it has been stated that the words "solvent" and "thinners" are synonymous in their application in some industries. This is unfortunate and should be clarified. In simplest terms, solvent as applied to industrial naphthas is a liquid which dissolves another substance. Industrial petroleum naphthas are solvents for gums, resins, and greases. Water is a solvent for salt and sugar. Methyl alcohol is a solvent for shellac, and ethyl acetate a solvent for nitrocellulose. A solvent which will readily dissolve a certain specific substance may have no solvent effect on another substance.

As applied to industrial naphthas, a thinner is defined as a liquid which may be employed to extend a solution but which does not materially impair the power of the solvent. This is illustrated by the use of thinners in such consuming industries as the paint, lacquer, and varnish, where the thinner is used to reduce the viscosity of the end product. A diluent is differentiated from a solvent or thinner in that it is employed to extend a solution but in doing so definitely weakens the power of the active solvent.

CHEMISTRY OF INDUSTRIAL NAPHTHAS

Industrial naphthas, as presently produced and distributed to industry, range from relatively pure to complex mixtures of hydrocarbons, i.e., chemical combinations of hydrogen and carbon derived from petroleum or natural gas. Pentane, hexane, and heptane represent some of the industrially pure hydrocarbons produced largely from natural gas; while toluene and xylene are produced, in a high degree of purity, either from some aromatic type of crude oil or from the newer refining processes which chemically change the hydrocarbons used as charging stock to the process. The first

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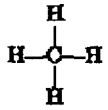
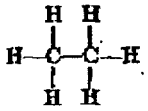
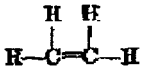
and simplest of these hydrocarbons is methane, or marsh gas, which is illustrated by the following formula:



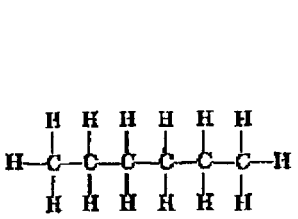
Methane is a gas under normal atmospheric conditions regarding temperature and pressure, and it is not a normal component of any industrial naphtha. It serves, however, to illustrate a normal hydrocarbon. In methane, carbon displays its normal valency, or chemical affinity, of 4 and hydrogen its normal affinity of 1. In other instances of the hydrocarbons, the carbon atom may have one or more of its valency values fulfilled by union with one or more other carbon atoms rather than with hydrogen. This can be illustrated by the next heavier hydrocarbon ethane, which also is a gas under normal atmospheric conditions. Its chemical formula is:



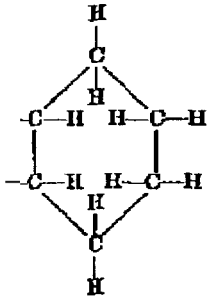
In the case of ethane, if we take away two of the hydrogen atoms, we have an illustration of still another group, or series, of hydrocarbons with a double, or unsaturated, bond between the carbon atoms. This group of hydrocarbons is known as the olefins, and these are found in industrial naphthas. The simplest of these olefin hydrocarbons, which is a gas, is shown in the following graphic formula:



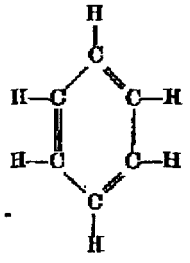
Carbon atoms may be linked together to form cyclic compounds in both saturated and unsaturated compounds. All these cyclic compounds are pertinent to industrial naphthas, since all are present in or components of these naphthas. The lowest molecular size of hydrocarbon which includes all of the above-mentioned types and which is present in industrial naphthas is shown below in graphic form. It is to be noted that each contains six carbon atoms.



Normal hexane



Cyclohexane



Benzene

It will be apparent from the above simple illustration of the several types of hydrocarbons to be found in petroleum that an almost unlimited number of compounds is possible. In fact thousands of these compounds are known and recorded in scientific literature, while numerous others are established in theory. From this it is obvious that the subject of the chemistry of even the compounds found in the industrial naphthas would constitute quite a library and would be beyond the scope of this article. A basic understanding of the petroleum hydrocarbon types is essential to a study of the nature and properties of the industrial naphthas. To those in industry who may desire to go into the subject of types of hydrocarbons in greater detail, there are many fine reference publications in organic chemistry available to supply the needed data. As applied to industrial naphthas, special attention is called to nos. 1 to 4 of the reference material on page 11-20.

Four Semitechnical Classifications. Industrial naphthas, as currently produced and distributed to industrial firms in many lines, are usually highly complex mixtures of hydrocarbons, with the exception of the relatively pure compounds such as hexane or toluene. Therefore, they do not lend themselves to accurate scientific classification in many instances. They vary from the paraffin-type hydrocarbons to the aromatics, and in some cases, they may contain naphthenes and olefins. Through usage over the years, there have evolved a semitechnical classification and nomenclature which will be followed in this discussion. These classes are (1) aliphatics, (2) aromatics, (3) intermediates, (4) odorless. In some cases it is the practice to divide the aliphatics into paraffins and naphthenes.

It has already been stated that many naphthas are complex mixtures of hydrocarbons. This is mainly due to the type of crude oil from which the naphtha is produced and also, to a limited extent, to the degree of fractionation used when the naphtha is produced. Crude oils from different producing fields vary widely in their properties. Some crude oils, such as Pennsylvania grade, are highly paraffinic, while some West Coast crudes are predominantly aromatic. The results in terms of characteristics of naphthas produced from different crudes can be illustrated by the "hydrocarbon breakdown" of two commercial mineral spirits. That produced from a Mid-Continent crude had 57 per cent of paraffins, 32 per cent of naphthenes, and 11 per cent of aromatic compounds. The naphtha made from a West Coast crude oil was 25 per cent paraffinic, 45 per cent naphthenic, and 20 per cent aromatic.

In general, when the dominating hydrocarbons comprising an industrial naphtha are paraffinic and/or naphthenic, the naphtha is classified as an aliphatic. More specific, however, is the practice in industry of classifying the industrial naphthas based on their solvency. This is an arbitrary compromise but has proved practical in usage of these materials. The degree of solvency is determined by the Kari-Butanol test,[*,5] which is described below under laboratory tests. Those naphthas with a Kari-Butanol number of 45 or lower are classified as aliphatics and without regard to their chemical composition.

The aromatics, in industrial naphthas, include the industrial grades of benzene, toluene, and xylene, with solvency at No. 98 or higher as determined by the Kari-Butanol test. To the aromatic group we can also add a few special naphthas, such as the alkyl naphthalenes, which have Kari-Butanol solvencies comparable to toluene and xylene and find special application in the industrial field.

The intermediate group of industrial naphthas covers those straight-run and blended naphthas with Kari-Butanol solvency numbers between 45 and 98. The fourth classification, the odorless solvents, has been set up to cover a relatively new group of industrial naphthas. These have only recently appeared; and they are characterized, not by their solvency, but by being for all practical purposes free from odor.

The practice of many producers and distributors of industrial naphthas to market their products by trade name does not simplify the problem of identifying their classification. This difficulty is offset by the fact that most concerns publish complete specifications of their naphtha products, which benefit consuming industries by identifying their classification as well as in other ways. For the consuming industries,

[*] Superior numbers indicate references on page 11-20.

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one of the most valuable publications covering the field of industrial naphthas is *Circular* 751, published by the Scientific Section of the National Paint, Varnish and Lacquer Association, Inc.[6] The *Circular*'s Thinner Index lists complete the conventional tests for all the industrial naphthas and, in most cases, includes a hydrocarbon breakdown. The value of this reference is enhanced by the fact it is periodically revised and brought up to date.

MANUFACTURE OF INDUSTRIAL NAPHTHAS

We have noted elsewhere in this article the wide range of physical and chemical characteristics that go to make up the modern industrial naphthas. The fact that they range from relative low solvency to high solvency, from extremely volatile materials such as hexane to very high boiling materials, and from narrow to wide boiling ranges points up the complexity of the problems involved in their manufacture.

In the production of industrial naphthas, first consideration must be given to the raw materials from which they are produced, namely, the crude oil and the natural gasoline. These raw materials themselves, like the resulting naphthas, are highly complex mixtures of hydrocarbons and vary widely from field to field, in their chemical composition. Therefore, in order to maintain uniformity of product, the conventional practice is to segregate for processing the crude oil or natural gasoline from which the naphthas are to be produced.

The first process involved is that of distillation. In fact, for most of the better known aliphatics, such as mineral spirits, Stoddard solvent, and VM & P naphtha, distillation is the only process involved. In a few cases a sweetening treatment of the naphtha may be required to improve the odor of the product. The fact that only the distillation step in refining is required has been made possible through the great improvement in fractionating equipment now employed in modern refineries. In fact, in the distillation of natural gasoline to produce the relatively pure solvents of the paraffinic type, such as hexane, superfractionation is required. In superfractionation, products with boiling ranges of the order of 1 to 5°F are not unusual. The versatility of modern fractionating equipment makes it possible to produce naphthas of practically any boiling range that may be required in industry.

Frost[7] has presented in three articles a very comprehensive picture of the production of the aliphatic-type industrial naphthas, with particularly useful data on the crude oils used and on the physical and chemical properties of the resulting products, with the precise fractionation involved.

In producing aromatic and intermediate industrial naphthas, the refining techniques become more complex and involve the newer processes, such as catalytic cracking, catalytic reforming, alkylation, isomerization, polymerization, and thermal reforming, usually with variations of the processes in these general types. All these processes are primarily chemical in that the chemical make-up of the raw material charged to the process is changed. Practically all these processes were originally developed to produce high-antiknock motor fuel from low-antiknock charging stock. It is a fortunate circumstance and to the advantage of industry that these newer processes also produce many of the most important industrial naphthas.

We have noted elsewhere that the aromatic naphthas—benzene, toluene, and xylene—were originally produced as byproducts in the coking of coal. Historically, the credit for the first method of producing aromatics from petroleum must go to L. Edeleanu, a Rumanian chemist, when he discovered the fact that liquid sulfur dioxide had the property of dissolving the aromatic hydrocarbons in petroleum oils but had low solvency for the paraffinic and olefinic hydrocarbons. Rumanian crude oil is one of several found in the world with a naturally high aromatic content. The Edeleanu process still enjoys some use for the production of aromatic compounds.

Because of the magnitude of the subject, it is not within the scope of this article to discuss all these new processes in detail. It must be recognized, however, that they have made and are still making important contributions in supplying a wide range of industrial naphthas of high quality. A few generalizations can be made, however. Figure 11-1 is a simplified flowsheet of a modern petroleum refinery integrated with

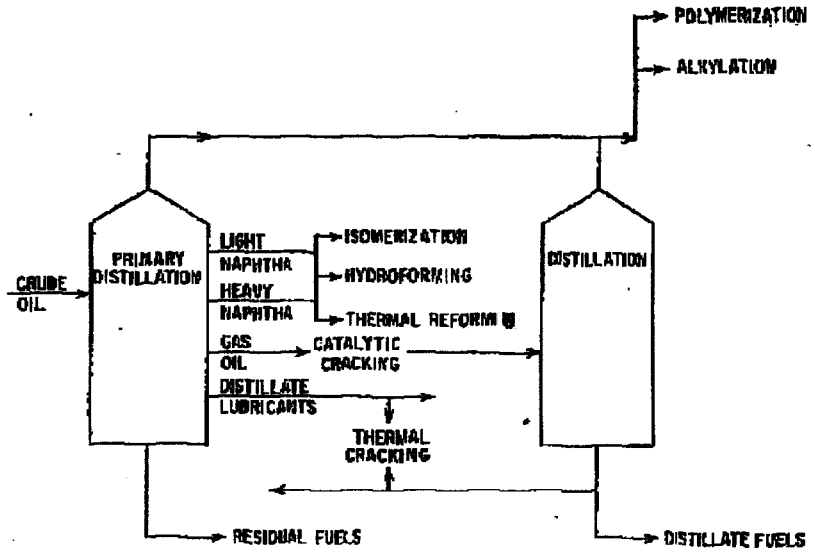

FIG. 11-1. Simplified refinery flow diagram for the production of industrial naphthas.

these several processes used in the manufacture of industrial naphthas. It serves to illustrate to some degree the interrelationship and complexities of modern plant operations, but it also indicates their versatility and flexibility. Two processes involved, thermal reforming and hydroforming, rate some additional attention because of their importance in relation to the production of industrial naphthas. Reforming is one principal source of the aromatics—benzene, toluene, and xylene—from petroleum. Hydroforming may be briefly described as a catalytic process which converts straight-run gasoline of paraffinic nature and low-antiknock properties into aromatic compounds largely through controlled dehydrogenation. From the overhead material from this operation, the light reformate, the aromatics—benzene, toluene, and xylene—are obtained. The hydroformer bottoms also have special interest in connection with industrial naphthas, as they consist of a high concentration of alkyl naphthalenes. These can be fractionated to produce several types of industrial naphthas with extremely high solvency. These particular naphthas have been found useful in the pesticidal field as solvents for insecticides, herbicides, and wood preservatives.

Alkylation is important in the production of industrial naphthas, as it is the process from which the newer odorless solvents are produced, such as odorless mineral spirits. This is a chemical process which can be simply illustrated by the word equation

$$\text{Isobutane} + \text{2-butene} \xrightarrow[\text{fluoride}]{\text{hydrogen}} \text{isooctane}$$

The residual products from this process are refractionated and treated to produce several odorless solvents. The naphthas from this process have improved odor

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treatment of paraffinic-type naphthas.

DISTRIBUTING METHODS MODERNIZED

The distribution of industrial naphthas in the past has followed no fixed pattern. Originally, owing to their nature as petroleum products, they were marketed through the normal sales outlets of the oil companies manufacturing them, along with the conventional petroleum products. In the past 25 years, however, a transition has been taking place, and the distribution of industrial naphthas is becoming more specialized. Many factors are involved in this change, the principal one being the recognition of the growing importance of the industrial naphthas as raw materials in the modern economy. Basically, the industrial naphthas occupy the same position as any other chemical raw materials in relation to the consuming industries. Therefore, the distribution of these products is tending to parallel more closely the distribution of industrial chemicals. A further factor in their distribution is the fact that it must be supplemented by technical sales service, again paralleling the methods used in the sale of chemicals.

There is no group of petroleum products that must be held to such strict and uniform specifications as the industrial naphthas. Therefore, in their distribution, the physical equipment, such as storage tanks, pumps, transfer lines, transporting equipment, and packages, must be strictly segregated for handling industrial solvents. This provides positive insurance against any mixing of the various naphthas, plus complete protection against any contamination of the materials from any source.

Because of the flammable nature of the industrial naphthas, many governmental agencies have established definite quantity and quality characteristics which must be met in their sale and distribution. One of the principal features of these regulations is to limit the quantities of the naphthas that may be carried in the consumer's inventory. Because of this provision, naphtha distributors must arrange for fast and frequent delivery service to their customers for these products. Industrial naphthas normally move in bulk quantities direct from the producing refineries by water, rail, or motor transport to terminal facilities strategically located in relation to the naphtha consumers. In the instance of large consumers, bulk shipments are made direct to storage at the consumers' plants. That these bulk shipments are growing is evidenced by the fact that normal tank-car bulk movement is now being supplemented by a large water movement in specially designed ocean-going vessels and in special barges on inland waterways. From these special industrial naphtha terminals, the naphthas are delivered in bulk and in less than carload lots to consumers either by the oil company direct or through jobbers and distributors. Generally the terminals are provided with special blending equipment, so that special naphthas can be "tailor-made" to the consumer's requirements. Waters[9] has outlined the direct effects in the blending of industrial naphthas.

The fact that the distribution of industrial naphthas is a specialized procedure has been recognized in industry, and many independent companies exist primarily to distribute these naphthas. In some instances the oil company which produces the naphtha has established a separate division to handle these sales or has set up a subsidiary company to carry on this work. A specific exception to the general practice has to do with the distribution of the best known industrial naphtha, mineral spirits, which is sometimes distributed in small quantities through the oil-company service stations. This is not general practice, however. All told, the current methods for distributing industrial naphthas are of a nature that assure the consumer uniformity of product in his requirements, supplemented by fast delivery service and essential technical assistance in the utilization of the product.

UTILIZATION AND STANDARDIZATION

In o modern industrial economy it is difficult to name an industry in wh industri naphthas are not directly or indirectly utilized. These products hav wide ar flexible range of qualities, such as solvency, distillation range, evaporati rates, s l so on, which makes them invaluable in many specialized industries. the acco panying group of three charts, Fig. 11-2 gives the boiling ranges of a rep

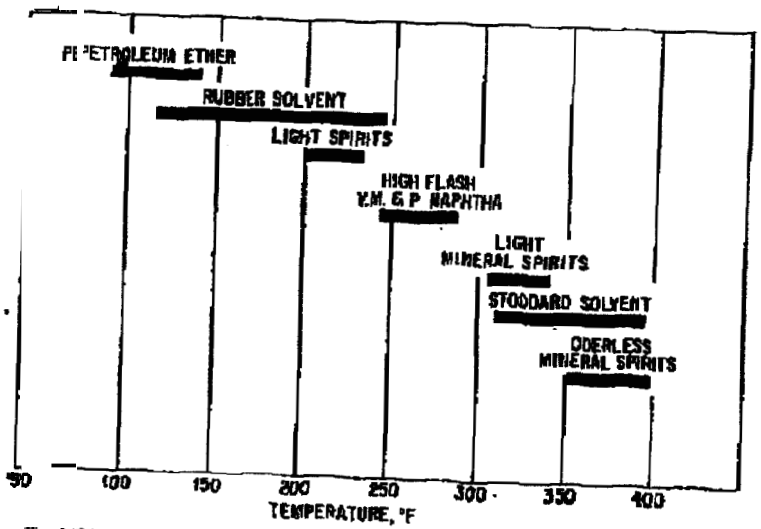

Fig. 11-2. Distillation ranges of a representative group of aliphatic naphthas.

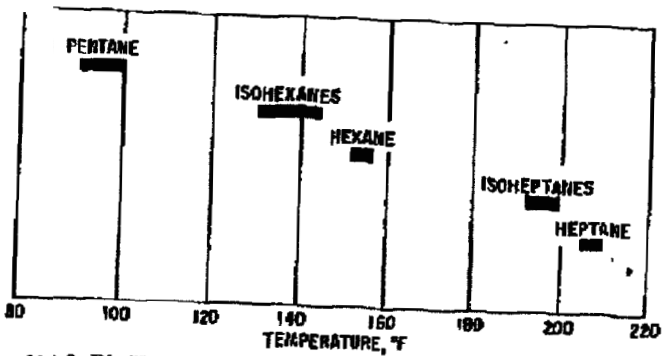

Fig. 11-3. Distillation ranges of a group of industrial paraffinic hydrocarbons.

sentative group of the most widely used aliphatic naphthas, based on data from reference 6. This shows both narrow- and wide-boiling-range naphthas varying from very volatile to higigh-boiling products. Figure 11-3 gives comparable data on a group of industrial puure paraffinic hydrocarbons, while Fig. 11-4 supplies similar data on a representativee group of aromatic naphthas. A further consideration in the wide use of the industrial naphthas is their ready availability in large volumes and their low cost relative tto that of similar products from other sources.

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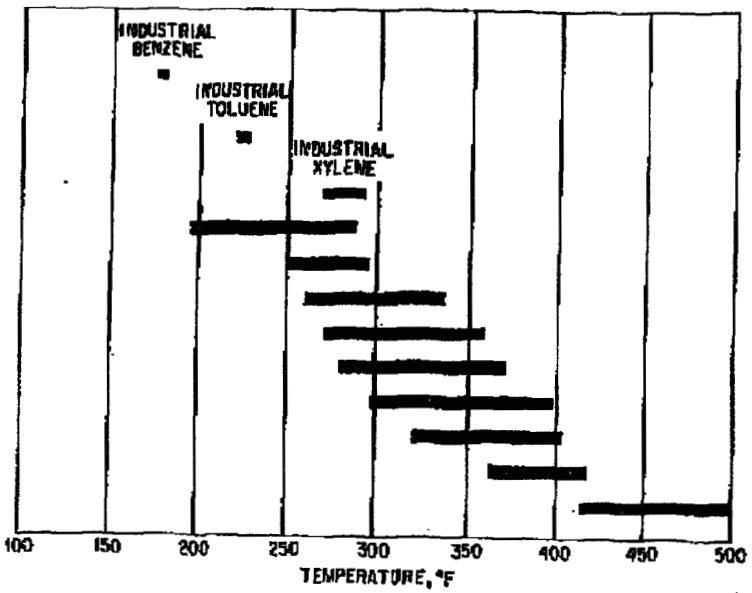

FIG. 11-4. Distillation ranges of three industrial aromatic naphthas.

The paint, varnish, and lacquer industry is one industry which is vitally dependent on industrial naphthas as a raw material. The unusually wide field of quality requirements demanded by this industry can be met in no other single group of solvents. This is a major subject in itself. References 6 and 9 to 15 inclusive contribute much valuable detail to the problem of the use of these products in this major industry. One of the more recent large-volume consumers of the industrial naphthas is in the pesticidal field, in the area of insecticides, herbicides, defoliants, and wood preservatives. The list of applications for the industrial solvents shown in Table 11-4 serves to illustrate the wide use of these products in many industrial fields.

Table 11-4. Typical Applications for Industrial Naphthas

Oil extraction	Dry cleaning	Textile manufacturing
Adhesives	Printing inks	Leather goods
Asphalt compounds	Rubber industry	Degreasing
Papermaking	Metal cleaning	Alcohol denaturant
Floor coverings	Resin extraction	Silicone compounds
Wax compounds	Type cleaning	Rustproofing compounds
Metallic dryers	Textile printing	Polishes
Chlorinated rubber	Machine cleaning	Undercoatings
Brake linings	Resin solutions	Chemical intermediates
Pharmaceuticals	Declutching solvents	

An examination of the specific application of some of the more widely used industrial naphthas also serves to illustrate their wide utility.

Hexane. This paraffin naphtha finds its greatest application in the extraction processes. Here it is used in the extraction of soya-bean oil, cottonseed oil, corn oil, castor oil, peanut oil, linseed oil foots, cocoa beans, sugar cane, and flaxseed and in the production of many essential oils. It is also used in the extraction of oils and fats from meat scraps, bones, garbage, wool, and greases. It finds a limited application in the manufacture of rubber cements and adhesives, intaglio inks, shoes, cellophane and masking tapes, and artificial-leather finishes and in the cleaning of precision mechanisms. It has the fastest evaporation rates of all the industrial naphthas.

Heptane. This is also a paraffinic naphtha and is used in the place of hexane when operating conditions require a high-flash solvent but with a slower evaporation rate.

Rubber Solvent. This low-boiling-point aliphatic solvent is used in the manufacture of rubber cements and adhesives, rubber tires, brake linings, intaglio inks, leather degreasing, paints, and lacquers.

Lacquer Solvent. As implied by the name, the principal use of this product is as a diluent in the preparation of lacquers and synthetic coatings, where a quick-drying material is required. Its evaporation rate is comparable to that of toluene, and it is frequently used in combination with toluene.

Varnish Maker and Painter's Naphtha (VM & P Naphtha). Its principal use is in thinning paints and varnishes and to some extent in lacquers. It is also employed in the manufacture of rubber cements, adhesives, waxes, and polishes and as type cleaner. It is frequently referred to as "light naphtha," "dry-cleaner naphtha," and "spotting naphtha."

Stoddard Solvent. This naphtha was originally developed as a special solvent for the dry-cleaning trade. It has good color and odor and a relatively high flash point. It also finds many uses in other industries, particularly metal cleaning and degreasing. Standard specifications for this naphtha have been set up by ASTM Committee D-2 on Petroleum Products and Lubricants. The requirements call for a "petroleum distillate, clear and free from suspended matter and undissolved water and free from rancid and objectionable odor. The odor shall be typical of a 'sweet' refined naphtha." Property requirements for Stoddard solvent are given in Appendix, page 11–25.

Benzene. This is the lowest boiling material in the aromatic series of naphthas. Because it is highly toxic, its use is more limited than the other aromatics and special precautions are required when it is employed. As a general rule, it should be used only when no other aromatic can do the job. From a volume standpoint its greatest use is as a raw material in manufacturing synthetic organic chemicals. Three grades of industrial benzene have been standardized by ASTM Committee D-16 on Industrial Aromatic Hydrocarbons and Related Materials, and their property requirements are given in Appendix A.

Toluene. When an industrial naphtha with high solvency is required, toluene is generally used. It is a solvent for the heavy synthetic resins and a thinner for synthetic resin coatings. It is one of the major components in the preparation of lacquers. Because of its rapid rate of evaporation, its use is indicated when fast drying is an important factor. Property requirements for two grades of industrial toluene are given in Appendix A.

Xylene. This naphtha, like toluene, has excellent solvency properties for many organic compounds and in particular the synthetic resins. It is used in most types of synthetic coatings. It has a slower evaporation rate than toluene and is used where slow-drying requirements cannot be met with toluene. Intermediate drying rates can be met by using a blend of xylene and toluene. Properties of four grades of industrial xylene are shown in Appendix A.

Among the relatively new aromatic naphthas being produced from petroleum, mention should be made of the alkyl naphthalenes. These solvents display some unusual properties, particularly for the pesticidal field, where the solutions of the active agents such as DDT, for example, must stand up in storage over long periods of time and through wide temperature ranges without precipitating the active agent. Furthermore, it is possible to supply these new naphtha products in a wide range of boiling points.

To date, 15 industrial solvents and related materials have been standardized and their specifications set up by the ASTM. These are listed in Table 11-5, and their properties given in Appendix A.

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Table 11-5. The Standardized Industrial Naphthas

Name	Specification Designation
Specifications Prepared by ASTM Committee D-2 on Petroleum Products and Lubricants	
Petroleum spirits (mineral spirits)	D 235
Heavy petroleum spirits (heavy mineral spirits)	D 983*
Stoddard solvent	D 484
Specifications Prepared by ASTM Committee D-16 on Industrial Aromatic Hydrocarbons and Related Materials	
Nitration-grade benzene	D 835
Industrial-grade benzene	D 836
Industrial 90 benzene	D 837*
Refined solvent naphtha	D 838
Crude light solvent naphtha	D 839
Crude heavy solvent naphtha	D 840
Nitration-grade toluene	D 841
Industrial-grade toluene	D 842
Nitration-grade xylene	D 843
Industrial-grade xylene	D 844
Five-degree xylene	D 845
Ten-degree xylene	D 846

* Tentative.

PHYSICAL AND CHEMICAL TESTS

Since the industrial naphthas are employed in a wide variety of consuming industries, it naturally follows that many laboratory test methods are used to evaluate their suitability for various applications. Many test procedures have been developed and standardized by such recognized technical organizations as the ASTM[16] and the Federation of Paint and Varnish Production Clubs.[17] Many producers of these naphthas as well as many consuming industries also have developed procedures for evaluating the naphthas to meet the requirements pertinent to their specific operations. The conventional laboratory test methods with which the oil industry is familiar in many instances are not applicable in determining the specific requirements for the industrial naphthas. In this limited text only the tests commonly used and their significance can be discussed. References 4 and 18 to 20 are recommended for wider and more detailed information on the laboratory evaluation of the industrial naphthas. Also, for more complete information on the standardized tests and their significance reference 21 will be valuable.

Gravity and Density. The density of industrial naphthas is normally indicated by specific gravity or by API gravity.[21] Specific gravity as applied to naphthas is the ratio of the weight of a given volume of the material at 60°F temperature to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air. The API gravity of a naphtha is based on an arbitrary hydrometer scale which is related to specific gravity as based on the following formula:

$$\text{Degrees API} = \frac{141.5}{\text{sp gr } 60/60°\text{F}} - 131.5$$

An API gravity of 10.0° is equivalent to a specific gravity of 1.0. Products heavier than water will have an API gravity decreasing from 10.0° as the specific gravity increases. Those naphthas lighter than water will have API gravity values increasing above 1.0° as the specific gravity decreases.

The primary use of either the specific-gravity or the API-gravity tests is to establish volume-temperature and volume-weight relationships which are essential in commercial transactions between suppliers and consumers. These relationships are particularly advantageous for those consuming industries whose formulas are established on a pound basis rather than a gallon basis although their purchases are on a pound basis. A convenient and accurate method for making the necessary volume-temperature and -weight relationships is by reference to the ASTM-IP Petroleum Measurement Tables, ASTM D 1250.[18] For more accurate measurement tables for use with benzene, toluene, and xylene, a new method has been developed by the ASTM and published for information only.[22]

The specific gravity of naphthas can be determined by the following ASTM standard methods of test.[23]

1. Density and Specific Gravity of Liquids by the Bingham Pycnometer, ASTM D 1217.

2. Density and Specific Gravity of Hydrocarbon Liquids by the Lipkin Bicapillary Pycnometer, ASTM D 941.

The API gravity of industrial naphthas can be determined by the ASTM Method for API Gravity of Petroleum and Its Products, ASTM D 287. ASTM D 1298, ASTM Standard Method of Test for the Specific Gravity of Petroleum and Its Products,[19] can also be referred to.

Color. The color of an *industrial naphtha is important to both consumer and producer.* For the former it is a determining factor of quality in respect to its effect upon the end product, such as white coatings. This is particularly true in the paint, varnish, and lacquer industry and in the dry-cleaning business. To the producer color is a partial indicator of the degree of refinement of the product.

For those naphthas having a "water-white" to "straw" color, the color is determined by the ASTM Tentative Method of Test for Saybolt Color of Refined Petroleum Products, ASTM D 156-53T.[20] It should be noted that, in normal commercial usage, an industrial naphtha with a color of +21, under the above procedure, is considered to be a water-white product.

For those naphthas having a color darker than pale straw, the color is determined by the ASTM Tentative Method of Test for Color of Lubricating Oils and Petrolatum, i.e., union colorimeter, ASTM D 155-45T.[15] The ASTM Color Standard, D 155-45T, can be compared directly with the National Petroleum Association (NPA) Standards by Table 11-6, which covers the color range involved.

Table 11-6. Color Standards for Naphthas

ASTM No. (D 155-45T)	NPA Name
1	Lily white
1.5	Cream white
2	Extra pale
2.5	Extra lemon pale
3	Lemon pale
3.5	Extra orange pale
4	Orange pale
4.5	Pale
5	Light red
6	Dark red
7	Claret red
8	.....

Volatility. The inherent volatility of the naphtha is perhaps the major quality that must be considered in any application for industrial purposes. This consideration, plus the fact that many regulations pertaining to volatility have been adopted, particularly by municipalities, to minimize fire and explosion hazards, has resulted in the development and standardization of several laboratory procedures for evaluating volatility. The first of these, and one with pertinent legal significance, is the flash point.

The flash point of an industrial naphtha may be defined as the lowest temperature, expressed in degrees Fahrenheit, at which the solvent will vaporize to such an extent as to form a flammable mixture with air. The flash point provides a qualitative index of fire and explosion hazard and also the necessary information for the correct transportation classification and labeling, as well as for the selection of the shipping container. Several procedures for flash-point determination are available.

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The determination of the flash point is carried out by heating a sample of the naphtha in a specification cup and passing a small flame over the surface of the liquid while heating. The temperature at which a flash, i.e., ignition of the vapors, occurs is recorded as the flash point. The standard cup may be of the open-cup type or provided with a cover (closed cup). The three standard procedures of test for the determination of flash point are:

1. ASTM closed cup (Tag closed cup), ASTM D 56.[10] This procedure is normally used for naphthas flashing below 175°F (79.44°C).

2. Pensky-Martens Closed Cup, ASTM D 93.[10] This standard test is designed for determining the flash point of No. 2 and heavier fuel oils. Therefore, its application to industrial naphthas at the most would be limited to a few special and unusually high boiling point products.

3. Cleveland Open Cup Method, ASTM D 92.[10] This is intended for determining the flash point, as well as the fire point, of all petroleum products, except fuel oils and those products having an open-cup flash point below 175°F (79.44°C).

Another method for determining flash point of naphthas is important and has government approval and therefore some legal status, although it has not yet been standardized. This is the Tag open-cup method. It should be noted that this procedure is currently under study by the ASTM, with a possibility of its eventual standardization. This procedure is designed for determining flash points of volatile, flammable materials having flash points above 60°F (15.56°C) and below 175°F (79.44°C). The test is not applicable outside this range. The importance of this test lies in the fact that, through long usage, it has been designated by governmental agencies as the test to use to determine proper transportation classification of material and labeling, under Interstate Commerce Commission regulations, as well as proper storage conditions under various governmental laws and regulations.

The distillation range is of major importance in considering the ultimate application of industrial naphthas, since it supplies a relative indication of the evaporation rate of one naphtha vs. that of another. The distillation range of the aliphatic naphthas is normally determined by ASTM D 86, while the boiling range of the aromatics—benzene, toluene, and xylene—is determined by ASTM D 850. Under both these methods there are two terms, both widely employed by the naphtha-consuming industries, which should be defined in order to eliminate misunderstandings that sometimes appear. These terms are "end point" and "dry point." Clarification of these terms avoids misunderstanding and confusion. It appears logical to point out that, owing to the many tests involved in evaluating the industrial naphthas, in any formal contractural obligations for the purchase or sale of industrial naphthas, it is highly desirable to include the specific test procedures to be used in determining the quality specifications that may be a part of the contract. This applies to other properties as well as the distillation range.

The ASTM[21] defines "end point" or "maximum temperature" as the highest thermometer reading observed during the distillation of the product under test. The same authority defines "dry point" as the thermometer reading at the instant the distillation flask used in the test becomes dry. ASTM D 1078 is a special distillation procedure for determining the distillation range of lacquer solvents[20] and other products with boiling ranges between 80 and 482°F. Several of the very volatile naphthas derived from natural gasolines are so volatile that they must be handled, measured, condensed, and recovered at lower temperatures than the higher boiling naphthas. For these products a special procedure for determining boiling range has been standardized, ASTM D 216.[19]

The ASTM has published, for information only, a test procedure[21] for determining the boiling range of petroleum products which, if ultimately standardized, will replace the present standard ASTM D 86 and D 158. This method is intended for use in the distillation of motor and aviation gasoline, naphthas, kerosine, gas oils, distillate fuel oils, and similar petroleum products. It is not intended for use with petroleum products of extremely wide distillation range. In the past various laboratories have experienced deviations in determining distillation ranges of the same product by the different ASTM distillation test methods. A cooperative interlaboratory study of the two ASTM methods has resulted in these conclusions:

(a) Size of flask, distillation rate, heating equipment and product boiling range have little or nothing to do with the errors noted between distillation methods D 86 and D 1078.

(b) The only source of error between the two methods lies in the thermometers used. When suitable corrections are made, the errors disappear.

(c) The wide divergence in boiling ranges between Methods D 86 and D 1078, as prognosticated for mineral spirits, in reality does not exist.

(d) The final boiling point should be eliminated as a specification limit for solvents.

The working group which made this interlaboratory study, of Subcommittee V, ASTM Committee D-1, concluded their report with these recommendations:

(a) That Method D 1078 be revised to eliminate from the scope the sentence, "This method is not intended to be used for mineral spirits and similar petroleum products."

(b) That all solvents under the jurisdiction of ASTM Committee D-1 be distilled in accordance with Method D 1078.

(c) That all solvent specifications under ASTM Committee D-1 jurisdiction be revised to include a specific partial immersion thermometer recommendation.

(d) That, when Stoddard Solvent is to be sold or used as Mineral Spirits, the ASTM D 86 distillation range be corrected for emergent stem temperature and be reported as such.

(e) That the 200 ml. flask used in Distillation Method D 850 and D 1078 be recommended to ASTM Committee D-2 as a suitable replacement for the present 100 ml. flask or the proposed 125 ml. MCA flask.

The characteristic of volatility must also include reference to the vapor pressure of industrial naphthas, since together with flash point, it is an important index of fire or explosion hazard in the transportation, handling, storage, and usage of this material. Vapor pressure, as determined by the standard ASTM method D 323,[10] provides data on vapor pressure.

The evaporation rate is another important characteristic of industrial naphthas. It is related to volatility and is of great significance to many consuming industries, since it provides the information on the time required for any specific naphtha to dry completely. Many variable factors are involved in any determination of evaporation rate, such as the temperature of the surrounding air, the atmospheric pressure, relative humidity, vapor pressure of the solvent at its boiling point, and heat of vaporization, among others.[22] Several test procedures for determining this characteristic of evaporation rate have been developed and are in use today. However, because of the complexities involved, no method as yet has been standardized. Therefore any given set of evaporation rates for naphthas is of little value unless the method by which they have been determined is also specified. An investigation of this problem is being carried out by Technical Subcommittee No. 66 of the New York chapter of the Federation of Paint and Varnish Production Clubs.[22] Rubek,[1] Billmeier and Rittenhausen,[11] and others have made substantial contributions to the study of evaporation rates for the naphthas. The Amsco method[13] has been employed for many years.

The Amsco method for determination of evaporation rates, though it leaves much to be desired from a scientific standpoint, does have the advantage of being simple and inexpensive in design of the test equipment, is relatively fast in operation, and does provide comparative results. The equipment consists of a boxed chamber with a small exhaust fan and a revolving table to hold evaporating dishes for the samples under test. The evaporating dishes are equipped with tightly fitting covers to ensure

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no loss through evaporation while weighing samples. Ten milliliter samples are weighed in the evaporating dishes and then placed on the turntable, the fan started, and covers removed from the evaporating dishes. Weighings are made at approximate increments of 10 per cent loss in weight to final evaporation. The results are plotted with evaporation time, in minutes, against percentage weight evaporated.

Other methods for determining rate of evaporation, involving modification of the Jolly balance, have been developed for industrial use. In general, these methods indicate the percentage of unevaporated material at specified time intervals. The results can be plotted to give evaporation curves. One procedure of test, based also on the modified Jolly balance, has been developed by Cathman.[26] This procedure gives very accurate results, reportedly an accuracy of 1 per cent throughout the evaporation range on duplicate results. Still another method is the Shell thin-film evaporometer, developed by the Shell Oil Co. This is also of the modified Jolly balance type and is the instrument being used in the work of Technical Committee No. 66 of the Federation of Paint and Varnish Production Club.[12]

Solvency. The large volume of industrial naphthas employed by industry primarily as solvents emphasizes the importance of the various test procedures used in evaluating this characteristic. Unfortunately, no single or standardized test exists by which this property in naphthas can be determined. The reason for this is not difficult to understand when it is recognized that these products are hydrocarbons and range from the low-solvency aliphatics to the high-solvency aromatics, not to mention the almost limitless number of materials for which industry must have solvents. In many instances, individual companies have developed methods for determining solvency tailored to meet their own particular requirements in these naphthas.

In determining solvency the following standard methods of tests are used, and they serve to indicate the qualitative and relative ability of a naphtha to hold in solution the more generally employed solutes and in particular those used in the protective coating industry.[28] All these tests are official ASTM methods:

1. Aniline Point and Mixed Aniline Point of Hydrocarbon Solvents, ASTM D-1012. This procedure is also approved by the Federation of Paint and Varnish Production Clubs.
2. Kari-Butanol Value of Hydrocarbon Solvents, ASTM D 1133, also approved by the Federation of Paint and Varnish Production Clubs.
3. Nitrocellulose Diluting Power of Hydrocarbon Solvents, ASTM D 1134.
4. Heptane Number of Hydrocarbon Solvents, ASTM D 1132.
5. Viscosity Reduction Power of Hydrocarbon Solvents, ASTM D 1311 (tentative).

As a generalization, it can be stated that the higher the aromatic content of an industrial naphtha, the greater the solvency. Therefore, an analysis of the naphtha, or a so-called "hydrocarbon breakdown," is highly desirable in determining the suitability of the material for certain specific applications. Several standardized procedures to indicate the nature of the hydrocarbons present are listed here:

1. Benzene and Toluene by Ultraviolet Spectrophotometry, ASTM D 1017.
2. Aromatic Hydrocarbons in Olefin-free Gasoline by Silica Gel Adsorption, ASTM D 936.
3. Hydrocarbon Types in Liquid Petroleum Products, ASTM D 1319.
4. Olefinic plus Aromatic Hydrocarbons in Petroleum Distillates, ASTM D 1018.
5. Olefins and Aromatics in Gasoline, D 875.
6. Refractive Index and Refractive Dispersion of Hydrocarbon Liquids, ASTM D 1218.

Two Tests for Detecting Sulfur. Because of the efficiency of modern manufacturing and refining processes, the possibility of obtaining industrial naphthas containing harmful elemental sulfur and corrosive sulfur compounds is rather remote. This is the case even if the original crude oil from which the naphtha was produced was a high-sulfur-type crude. Two nonstandardized tests for sulfur are widely used, namely, the so-called doctor test and the full distillation copper strip corrosion test. The former is a qualitative method for detecting the presence of mercaptan sulfur or hydrogen sulfide in the material. A naphtha that gives negative results with this test is designated as "sweet," i.e., having a good odor. The latter is used to indicate corrosion and is employed principally in the coating industry. An entirely adequate standard test is the ASTM D 130, Free and Corrosive Sulfur in Petroleum Products.[13]

The scope of this article on industrial naphthas does not permit a complete detailed discussion of the various test procedures or their significance. For this information the reader is directed to the ASTM *Book of Standards*.[14] For a complete discussion the significance of the various tests given here mostly by title, the reader is directed to the *ASTM Special Technical Publication* 7-B, Significance of ASTM Tests for Petroleum Products.[31]

SAFETY PRECAUTIONS ESSENTIAL

In the use of industrial naphthas, consideration must be given to their inherent properties and the necessary precautions taken to assure maximum safety in their handling. These materials are flammable, and upon evaporation, under certain conditions, they will form explosive mixtures with air. Also it is important to consider the effect of these naphthas on human beings who may come into contact with the materials or vapors from them. Operators may be exposed to direct contact to the skin, through inhalation of the vapors, or orally. The resulting problems of toxicology have been studied by medical authorities with the oil companies, and reports are available in the literature. Only a few generalizations are within the scope of this discussion.

Of all the industrial naphthas, the aromatics are the most toxic and, therefore, rate the major protective precautions. The aliphatics, such as ordinary mineral spirits, are relatively nontoxic. Benzene is highly toxic, and great care must be exercised in its handling. Toluene and xylene are less toxic but more of this nature than the aliphatics. Direct skin contact with these naphthas may result in dermatitis. If the vapors are inhaled or absorbed through the skin, in extreme cases they may act as irritants, asphyxiants, or anesthetics. Some individuals display greater sensitivity to the industrial naphthas and may require greater safety precautions. Extensive publications on this subject of the toxicological properties of the naphthas are widely available. The *Toxicology Review*[30] published by the American Petroleum Institute are of special interest, since they stem from the petroleum industry. Various publications of the U.S. Public Health Service are authoritative sources of information. Some of the state industrial commissions have also published excellent material on the subject of safety. The American Conference of Governmental Hygienists is also a source of published material.

Many of the safety precautions taken to protect operators also serve to protect property against explosion and fire. The flammability of hydrocarbons is always a problem in the storing and handling of industrial naphthas. Many of these vapors are heavier than air, and therefore provision for exhausting vapors from working areas is necessary. In the areas where naphthas are stored or handled, adequate ventilation should always be provided. Leaking fittings, pumps, valves, and storage tanks should not be tolerated. Handling equipment should be of the type that will minimize spillage. Obviously, fires and lights should not be allowed in areas where naphthas are stored and used, and all electrical equipment should be of the approved explosionproof type. Table 11-7 presents for a few naphthas their hazards both for operators and for property. Column 1 in the table indicates the MAC (maximum allowable concentration) in air expressed in parts of naphtha per million parts of air

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Table 11-7. Relative Toxicity and Flammability Ratings for Selected Industrial Naphthas

Naphtha	Column 1 MAC*	Column 2†
Pentane	1,000	
Hexane	500	90–95
Heptane	500	
Octane	500	
Stoddard solvent	500	30–40
Gasoline	500	95–100
Kerosine	500	30–40
Naphtha (petroleum)	500	
Naphtha (coal tar)	200	
Benzene	35	95–100
Toluene	200	75–80
Xylene	200	40–45

* Maximum allowable concentration in air, expressed in parts of naphtha per million parts of air, from the American Conference of Governmental Hygienists.
† Flammability ratings of the Underwriters' Laboratories.

as taken from the American Conference of Governmental Hygienists, 1954. Column 2 indicates the Underwriters' Laboratory flammability ratings for the naphthas. The data is shown only to indicate roughly the relative toxicity and flammability of these materials. In column 1, the lower the MAC, the greater the toxicity, while in column 2 the lower the ppm, the less the fire and explosion hazard. In any specific application two factors relative to these conditions of toxicity and flammability should be kept in mind. First, with any industrial naphtha, as, for example, mineral spirits, while the material in its chemical composition will be predominantly made up of aliphatic hydrocarbons, it may vary considerably in its aromatic content, depending largely on the crude petroleum from which it was produced. In such a naphtha the one with the lowest aromatic content will show the lowest toxicity. Second, and again using mineral spirits as an example, the chemical composition as well as the boiling range must be considered in assessing its flammability characteristics. A safe general rule to follow is to overrate the maximum allowable concentration as to both toxicity and flammability and thus provide an ample margin of safety.

For the manufacturers of agricultural sprays and similar products using industrial naphthas, there may be another problem, that of "phytotoxicity," or toxicity to plants, trees, and shrubs. There are so many factors involved in this problem that only a generalization can be made in the light of present knowledge. In general, the higher the aromatic content of an industrial naphtha, the greater its phytotoxicity.

GUIDE TO CURRENT AND PRIMARY REFERENCE DATA

INDUSTRIAL NAPHTHAS

For titles of reports indexed below see Reference Data Directory, Part 1 of Sec. 16.

Sampling and Measurement. API-22, ASTM-3, ASTM-4.
Specifications and Properties. ASTM-1, ASTM-5, ASTM-10, ASTM-11, MPSA-1, NBS-2, NGAA-2.
Testing Methods. ASTM-1, ASTM-5, GPO-6, NPVLA-1.
Storage, Handling, and Transportation. API-25, API-34, BE-1, CG-2, NFPA-2, NFPA-5, NFPA-6.
Supply-Demand and Utilization. API-8, API-26, BM-16, MCA-1, USTC-1.
Sources of Supply. BM-8, MHPC-3, OGJ-1.
Prices and Price Trends. MHPC-1, OGJ-2, OPDR-1.
Special Taxes, Inspection. API-33, WPRA-1

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APPENDIX A. PROPERTIES OF STANDARD INDUSTRIAL NAPHTHAS AND RELATED MATERIALS

(Taken from the Standard Specifications Issued by the American Society for Testing Materials)

Prepared by ASTM Committee D-2 on Petroleum Products and Lubricants

Petroleum Spirits (Mineral Spirits), D 235

Scope. These specifications apply only to petroleum distillates.
Properties. The material shall conform to the following requirements:

Appearance	clear and free of suspended matter and water
Color	water white, not darker than No. 21 Saybolt Chromometer
Flash point, min.	100 F (38 C)
Blackening	shall not blacken or corrode clean metallic copper in 30 min. at boiling point of spirits
Distillation:	
Percentage recovered at 350 F (177 C), %	50
End point	410 F (210 C)
Acidity of distillation residue	neutral

Heavy Petroleum Spirits (Heavy Mineral Spirits), D 365*

Scope. These specifications apply only to petroleum distillates used as thinners for slow-setting paints and varnishes.
Properties. The material shall conform to the following requirements.

Appearance	clear and free of suspended matter and water
Color	water white, not darker than No. 21 Saybolt Chromometer
Flash point, min.	125 F (51.5 C)
Blackening	shall not blacken or corrode clean metallic copper in 30 min. at boiling point of spirits
Distillation:	
Initial boiling point, min.	340 F (171 C)
95 per cent (by volume)	460 F (238 C)
End point, max.	495 F (231.5 C)
Acidity of distillation residue	neutral

* Tentative.

Stoddard Solvent, D 484

Scope. These specifications cover a grade of petroleum distillate of low flammability used in dry cleaning.
General Requirements. Stoddard solvent shall be a petroleum distillate, clear and free from suspended matter and undissolved water, and free from rancid and objectionable odor. The odor shall be typical of a "sweet" refined naphtha.

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Detailed requirements. Stoddard solvent shall conform to the following detailed requirements:

Color	water-white or not darker than 1[1]
Corrosion at 100 C	not more than extremely slight discoloration of the copper test strip, or shows no greater corrosion than a mutually approved reference strip
Doctor test	negative
Sulfuric-acid absorption, max., per cent	5
Flash point, min., deg. Fahr.	100
Distillation:	
Percentage recovered at 350 F (176 C), min	10
Percentage recovered at 375 F (190 C), min	90
End point, max., deg. Fahr.	410
Residue, max., per cent	1.5
Acidity	no acid reaction to methyl orange shown by residue from distillation

Containers. Stoddard solvent shall be delivered in clean containers or tanks. If container previously has been used for other materials, such as fuel oil, etc., it shall be thoroughly cleaned and rinsed with Stoddard solvent.

Prepared by ASTM Committee D-16 on Industrial Aromatic Hydrocarbons and Related Materials

[redacted] de Benzene, D 835

Properties. Nitration-grade benzene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.8820 to 0.8860
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Total distillation range at 760 mm. pressure, for any one sample	not more than 1 C, including the temperature of 80.1 C
Solidifying point	not lower than 4.85 C (anhydrous basis)
Acid wash color	not darker than No. 2 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Industrial-grade Benzene, D 836

Properties. Industrial-grade benzene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.875 to 0.886
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Total distillation range at 760 mm. pressure, for any one sample	not more than 2 C, including the temperature of 80.1 C
Acid wash color	not darker than No. 3 color standard
Acidity	no free acid, that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Industrial 90 Benzene, D 837[a]

Properties. Industrial 90 benzene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.870 to 0.885[b]
Color	not darker than 20 on the Platinum-Cobalt scale by ASTM Method D 1209, or the visible color shall be not darker than standard by Method D 853.
Distillation range at 760 mm. pressure:	
Initial boiling point (first drop), min	78 C
Percentage recovered at 100 C, min	90
Dry point, max.	120 C
Nonvolatile matter, max.	0.005 g per 100 ml
Odor	characteristic aromatic hydrocarbon odor as agreed on by buyer and seller
Acid wash color	Not darker than No. 6 color standard
Water	not sufficient to show turbidity at 20 C
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Corrosion (copper strip)	copper strip shall not show iridescence nor a gray or black deposit or discoloration

[b] Equivalent specific gravity, 20/20 C = 0.866 to 0.882. In case of dispute, experimental values for 15.56/15.56 C shall be controlling.

[a] Tentative.

Refined Solvent Naphtha, D 836

Properties. Refined solvent naphtha shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.850 to 0.870
Color	not darker than a solution of 0.0050 g of $K_2Cr_2O_7$ in 1 liter of water
Distillation range at 760 mm. pressure:	
Percentage recovered at 130 C	not more than 5
Percentage recovered at 145 C	not less than 90
End point (dry point)	not above 155 C
Acid wash color	not darker than No. 10 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2

Crude Light Solvent Naphtha, D 839

Properties. Crude light solvent naphtha shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.860 to 0.885
Color	light amber
Distillation range at 760 mm. pressure:	
Percentage recovered at 150 C	not more than 5
Percentage recovered at 160 C	not less than 90
End point (dry point)	not above 180 C
Acidity	no free acid; that is, no evidence of acidity

Crude Heavy Solvent Naphtha, D 840

Properties. Crude heavy solvent naphtha shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.885 to 0.970
Color	between light amber and dark red
Distillation range at 760 mm. pressure:	
Percentage recovered at 150 C	not more than 5
Percentage recovered at 165 C	not less than 5
Percentage recovered at 200 C	not less than 90
End point (dry point)	not above 230 C
Acidity	no free acid; that is, no evidence of acidity

Nitration-grade Toluene, D 841

Properties. Nitration-grade toluene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.8660 to 0.8730
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Total distillation range at 760 mm. pressure, for any one sample	not more than 1 C, including the temperature of 110.6 ± 0.1 C
Paraffins	not more than 1.5 per cent by volume
Acid wash color	not darker than No. 2 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

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Industrial-grade Toluene, D 843

Properties. Industrial-grade toluene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.864 to 0.874
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Total distillation range at 760 mm. pressure, for any one sample	not more than 2 C, including the temperature of 110.6 C
Acid wash color	not darker than No. 4 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Nitration-grade Xylene, D 842

Properties. Nitration-grade xylene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.8650 to 0.8709
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Distillation range at 760 mm. pressure:	
Total distillation range for any one sample	not more than 3 C, including the temperature of 139.3 C
Initial distillation temperature (first drop)	not below 137.2 C
End point (dry point)	not above 140.3 C
Paraffins	not more than 4.0 per cent by volume
Acid wash color	not darker than No. 6 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Industrial-grade Xylene, D 844

Properties. Industrial-grade xylene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.850 to 0.870
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Distillation range at 760 mm. pressure:	
Percentage recovered at 130 C	not more than 5
Percentage recovered at 145 C	not less than 90
End point (dry point)	not above 155 C
Acid wash color	not darker than No. 10 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Five ⟵ Xylene, D 845

Properties. Five-degree xylene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.860 to 0.870
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Distillation range at 760 mm. pressure:	
Total distillation range for any one sample	not more than 5 C, including the temperature of 139.3 C
Initial distillation temperature (first drop)	not below 137 C
End point (dry point)	not above 143 C
Acid wash color	not darker than No. 6 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

Ten-degree Xylene, D 846

Properties. Ten-degree xylene shall conform to the following requirements:

Specific gravity, 15.56/15.56 C	0.860 to 0.870
Color	not darker than a solution of 0.0030 g of $K_2Cr_2O_7$ in 1 liter of water
Distillation range at 760 mm. pressure:	
Total distillation range for any one sample	not more than 10 C
Initial distillation temperature (first drop)	not below 135 C
End point (dry point)	not above 145 C
Acid wash color	not darker than No. 6 color standard
Acidity	no free acid; that is, no evidence of acidity
Sulfur compounds	free of H_2S and SO_2
Copper corrosion	copper strip shall not show iridescence nor a gray or black deposit or discoloration

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Table 11-22. Examples of Applications of Oils for Selective, Postemergence Weed Control in Crops

Crop	Petroleum product	Gal per acre
Beets	Stoddard solvent or aromatic oils	80
		30
Berries	Diesel fuel	40
Carrots	Stoddard solvent	60
Celery	Stoddard solvent	80
Cotton	Stoddard solvent	15
Cranberries	Kerosine	300
Flax	Stoddard solvent and kerosine	80
Grapes	Diesel fuel, aromatic oils	10
Onions	Stoddard solvent	80
Orchards	Diesel fuel	
Parsnips	Stoddard solvent	60
Soya beans	Stoddard solvent	5

320°F, API gravity of 48 to 50°, and aromatics content of 10 to 17 per cent were employed. Savings were estimated to be 40 to 90 per cent of the cost of hand weeding.[56] Of the herbicidal oils reported by the California Department of Agriculture,[13] five samples had an unsulfonated residue of less than 20 per cent, 16 between 20 and 39 per cent, 34 between 40 and 60 per cent, and 11 over 60 per cent.

FUNGICIDES

Although petroleum oils have long been used as horticultural insecticides, it is only recently that their value as a fungicide has been realized. In experimenting with the use of oil as a carrier for fungicides in low-volume (1 to 2 gal per acre) mist spraying, Guyot and Cuille[57,58] discovered that oil by itself controlled the Sigatoka disease of banana plants. The fungus (*Mycosphaerella musicola* Leach) responsible for this disease attacks the leaves of the plant. Bordeaux mixture has been used to control Sigatoka but is being replaced by oil misting, since the latter is both cheaper and more effective. The Standard Oil Co. (New Jersey) has been active in developing superior banana spray oils and in spreading the use of this technique throughout the banana-growing areas. The oil is applied in the form of a fine mist (50 to 100 microns) approximately 1 gal per acre every 2 or 3 weeks. Frequent application is necessary in order to protect the new leaves which develop throughout the growing period of the banana plant. Both light, portable mist sprayers and aircraft are used to apply the oil.

Tobacco Desuckering. In 1949, D. B. Anderson of North Carolina State College discovered that white mineral oil which he was using as a carrier for growth regulators controlled suckers on tobacco better than those with the chemicals. It was found[59] that emulsified white mineral oil was as effective and considerably more resistant against soft rot. Heavier (i.e., higher viscosity) oils were found to be more successful.[60] The oil is applied as an approximately 50 per cent emulsion to the top of the stem at the time the plant is topped. About 2 or 3 mils are used. Devices are used which top the plant and apply the proper quantity of oil. The oil prevents the growth of suckers which normally grow in the axils of leaves below the portion topped. Maleic hydrazide was used to a considerable extent in 1957, but there are indications that this is not so satisfactory as oil, and it is probable that use of oil will increase.

SOLVENTS FOR AGRICULTURAL PESTICIDES

Prior to World War II, agricultural applications of pesticides consisted of dusting and spraying solutions or suspensions. The products used were chiefly inorganics, such as arsenicals, copper, and su none, and nicotine; and orchard residue oil was the active insecti cultural pesticide field. The tre application by spraying has em otherwise, in this field of pesticid

Emulsion concentrates consist together with an emulsifier. A contain the highest possible conc fier is important. It should be may be satisfactory for two to toxicant produces better emulsio of the emulsion.

Obviously, the most importan is its ability to dissolve a suffic must also retain the solute at te varies with the pesticide employ all petroleum solvents. On the Some products are manufactur stability is unimportant. Othe be carried over the winter and

Safety. The solvent must b factors, and each is relative to If the product is used in a hou the other hand, if the product parathion, any slight toxicity o

The product should present household sprays or aerosols, th This is likewise true of airpla hazard. On the other hand, water, fire hazard while spray be used. Of course, there wo

The product should not inju chief disadvantages of the use the fact that, if they are not p plant may result. All aromati concentrations. Applied dire as herbicides, actually killing

There is much we do not kno least two factors affect the ph the boiling range of the aromat probably owing to the length

Other Characteristics. Col household products. Howeve formulations. Strong odors a of crops. Color is of no conse Low specific gravity is desirab tant. If products are sold on the cost. A 25 per cent DDT in a heavier solvent, 2.1 lb ma gravity solvents produce emul tend to cream to the bottom, Some government specificati

·cise any desired options offered herein.

s, of the issues in effect on date of invitation chases made under this specification by the

, Standard Specification for Marking Ship-

:ifications for Inspection of Material.

n the contract or order, each shipping con- equirements of U. S. Air Force Specification Container, Domestic and Export Shipment,

quirements, Gasoline, Unleaded

	Test Limits
.....	158
.....	266
.....	365
.....	2
max.....	10
.....	4
in*.....	62
.....	0.25
.....	None
.....	480
.....	15

specifies that the unleaded gasoline will be used nber requirement may be waived.

eir ASTM Equivalent, Gasoline, Unleaded

	Method	ASTM equivalent
.....	100.1	D 86
.....	120.1	D 323
.....	330.2	D 381
.....	600.1	D 357
.....	520.1	D 90
.....	530.2	D 130
.....	550.1	D 526
.....	535.2	D 525
.....	900.1	D 206
.....	40.1	D 287
.....	10.1	D 156

ard temperature of 60°F as specified in the contract y for selection of the proper group in the volume

KEROSINE; VV-K-211c, MARCH 24, 1952, INCLUDING AMENDMENT 1, SEPTEMBER 18, 1956

1. Classification

1.1. **Grade.** Kerosine covered by this specification shall be of but one grade.

2. Applicable Specifications and Other Publications

2.1. **Specification.** The following Federal Specification, of the issue in effect on date of invitation for bids, forms a part of this specification:

VV-L-791—Lubricants, Liquid Fuels, and Related Products; Methods of Sampling and Testing

2.2. **Other Publication.** The following publication of the issue in effect on date of invitation for bids, forms a part of this specification:

Code of Federal Regulations, Title 49, Transportation, Chapter 1, Interstate Commerce Commission, Parts 71-78; Explosives and Other Dangerous Articles—49 CFR 71-78.

2.3. Specifications and other publications applicable only to individual departments are listed in section 7.

3. Requirements

3.1. **Material.** The kerosine shall be a petroleum fraction, shall be free from water, additives, foreign and/or suspended matter, and shall be suitable for use as an illuminating oil.

3.2. **Burning.** The kerosine shall conform to the following burning test requirements. (See 4.3)

3.2.1. *Time of Burning.* Unless otherwise specified, a minimum of 16 hours continuous burning after the first weighing shall be required (see Table II, page 16-34).

3.2.2. *Rate of Burning.* After the first weighing, the rate of burning shall not be greater than 29 ml. per hour with the I. P. burner or 46 ml. per hour with the A.S.T.M.-27 burner (see Table II).

3.2.3. *Appearance of Chimney at End of Test.* The chimney shall be clean or only slightly clouded.

3.2.4. *Condition of Wick at End of Test.* The wick shall have no appreciable hard incrustation.

3.2.5. *Flame Characteristics at End of Test.* The flame shall not be smoky and shall be practically as large at the end of the test as when the final adjustment of the wick was made.

3.3. **Physical and Chemical Requirements.** The kerosine shall conform to the physical and chemical requirements shown in Table I.

4. Sampling, Inspection, and Test Procedures

4.1. **Sampling.** Sampling shall be in accordance with method 300.1 of Federal Specification VV-L-791.

4.2. **Place of Inspection.** Unless otherwise specified, inspection shall be made at the point of delivery in accordance with method 950.1 of Federal Specification VV-L-791.

4.3. **Test.** Tests shall be performed in accordance with the methods described in Federal Specification VV-L-791, as shown in Table II.

4.3.1. *Color*

4.3.1.1. The oil to be tested shall be filtered through qualitative filter paper to remove any moisture or foreign matter that may be present. About 100 ml. of the filtered oil shall be placed in each of two chemically clean and dry 4-ounce bottles.

4.3.1.2. The bottles containing the filtered oil, loosely stoppered with clean new corks, shall be placed in the constant temperature bath maintained at 212°F. At the end of ½ hour, the cork stoppers shall be pressed down firmly, and the bottles and contents allowed to remain in the bath for a total period of time of 16 hours.

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4.3.1.3. At the end of the 16-hour heating period, the bottles containing the oil shall be removed from the bath and allowed to cool in a dark place to room temperature.

4.3.1.4. The colors of the two samples of heat-treated oil shall be determined in accordance with method 10.1 of Federal Specification VV-L-791. If the results differ by more than four numbers they shall be considered unsatisfactory and the test shall be repeated. If satisfactory, the mean of the two determinations shall be recorded.

5. Preparation for Delivery

5.1. Packaging. Unless otherwise specified, commercial packaging is acceptable, if in accordance with the Interstate Commerce Commission regulations for the transportation of explosives and other dangerous articles.

5.2. Packing. The subject commodity shall be prepared for shipment to permit acceptance by carrier for transportation at the lowest applicable rate, and to afford maximum protection from normal hazards of transportation. Packing must be in accordance with the Interstate Commerce Commission regulations.

5.3. Marking. Unless otherwise specified, shipping containers shall be marked with the name of the material and the quantity contained therein, the specification number, the name of the contractor, and the number of the contract or purchase order. Marking shall be in accordance with the Interstate Commerce Commission regulations.

6. Notes

6.1. Intended Use. Kerosine covered by this specification is intended for use as an illuminating oil in wick-fed lamps. It is also suitable for cooking, heating, and for other purposes.

Table I. Physical and Chemical Requirements, Kerosine

Flash point, °F min	115	
End point, °F; max.	571	
Sulfur, per cent max	0. 15	
Color, Saybolt chromometer no darker than	+ 21	
Color, Saybolt chromometer no darker than (after heating 16 hr)	+ 16	(See 4.3.1)
Burning test, hr, min	16*	
Cloud point, °F	5	

* When required, a minimum burning time exceeding 16 hr may be specified in the contract or order.

Table II. Methods of Test, Kerosine

Test	Method no.	ASTM equivalent
Burning quality	210.6*	D 187
Flash point	110.1	D 56
End point	100.1	D 86
Sulfur	526.1	D 90
	19.1	D 156
Color (after heating 16 hr)	See 4.3.1	
Cloud point	20.1	D 97

* The minimum burning time shall be 16 hr, unless otherwise specified. (See 6.2.)

FUEL OIL, DIE

1. Classification

1.1. Grades. The diesel fuel grades (see 6.1 and 6.2):
Grade DF-A—Arctic grade
Grade DF-1—Winter grade
Grade DF-2—Regular
Grade DF-4—Heavy

2. Applicable Specifications and

2.1. The following specificati
tion for bids, form a part of th

Federal Specifications:
VV-L-791—Lubricants, Li
Sampling, and Testing.
PPP-D-729—Drums; Met

Military Specification:
MIL-C-124—Containers (
Items).

Military Standard:
MIL-STD-129 BC1 (5 JA

2.2. Other Publications.
Unless otherwise indicated, th

Interstate Commerce Commi
49 CFR 71-78—Interstа
Transportation of Exp

American Society for Testin
ASTM Manual on Meas
ASTM Manual of Engin

3. Requirements

3.1. Physical and Chemica
and chemical requirements s
3.1.1. *Ignition Quality Test*
Table I may be obtained by
improver compounds (see 6.
carbon residue should be not
3.2. Statement of Analysi
contractor shall provide a s
required in Table I and a sta

4. Sampling, Inspection, an

4.1. Sampling. Samples
Manual on Measurement
number and disposition of t
4.2. When required by pu
pliance with the requiremen
4.3. Tests. All tests shal
4.3.1. *Additional Tests.*
be necessary to establish th