CHAPTER 21
HYDROCARBON SOLVENTS

Hydrocarbons derived from crude oil have been used as solvents and thinners in the industry since the first barrel of crude was distilled through a still. Over a period of time these petroleum solvents have partially or completely displaced many nonpetroleum solvents such as the turpentine or coal tar used earlier. The principal reason for the change to petroleum solvents was their larger production and lower cost. Nevertheless, some nonpetroleum solvents have superior performance in certain select applications. The use of nonpetroleum solvents continues, although their share in overall solvent usage has declined considerably.

NONPETROLEUM SOLVENTS

Gum Turpentine

Gum turpentine is made from distilling the resinous gum from pine trees. It has a distinctive strong odor and a fast evaporation rate, releasing harmful vapors that are absorbed through healthy skin. Turpentine is an effective solvent for oil, alkyd-based paints, varnishes, and for tar, grease, and tree sap. Turpentine has been the solvent used in oil painting for centuries. It blends beautifully with oil-based paints, varnishes, and enamels and ensures a smooth, even application. Gum turpentine usually contains a small amount of sticky residue, which can be imparted to painting if this kind of turpentine is used in large quantities. It may remain in layers of paint, inhibiting proper drying and in time causing discoloration. For these reasons, natural turpentine is becoming less commonly used in painting and art industries. Rectified or artist-grade turpentine is double distilled to remove the last traces of residue from pine tree gum. This product is ideal for oil paints and media because it does the job and then evaporates from paint film without a trace. Turpentine is also an essential ingredient in the mixture to create an antique oil finish on fine furniture.

Many substitute products have arrived in the market that essentially perform the same functions with less noxious vapors. These are generally petroleum distillates that evaporate quickly. They can cause filming of color in fine art painting and an uneven coverage if used as a thinner for house painting. These are less expensive alternatives, but to achieve excellent paint consistency and avoid rapid drying of other thinners, nothing else can outperform pure turpentine, which is still considered best for color quality, durability, and easy maintenance. Properties of gum turpentine and distilled turpentine are shown in Table 21-1.

PETROLEUM-BASED SOLVENTS

Petroleum-based solvents are widely used in a large number of industries because of their ready availability and lower cost. N-hexane is used as a solvent for the extraction of edible oils from oil seeds. Petroleum distillates are used as a solvent in the dry cleaning of garments and leather. The paint, varnish, and lacquer industry is a major consumer of petroleum distillates. Petroleum distillates are used in agriculture, as a vehicle for pesticides, insecticides, herbicides, defoliants, and wood preservatives. Table 21-2 shows some of the uses of petroleum-based solvents.

TABLE 21-1 Properties of Gum Turpentine and Distilled Turpentine

	Gum turpentine	Distilled turpentine
Specific gravity	0.864	0.864
Distillation range, °F	311–345	311–345
Flash point, °F	91	91
Evaporation rate (n-Butyl acetate = 1)	0.38	0.38
Kauri-butanol value (ASTM 1133)	64	64

TABLE 21-2 Typical Applications of Petroleum Solvents

Adhesives	Alcohol denaturant
Asphalt compounding	Chemical intermediates
Dry cleaning	Leather goods degreasing
Machine cleaning	Paper making
Polishes	Printing inks
Resin solutions; paints and varnish manufacture	Rosin extraction
Rubber industry	Silicon compounds
Textile manufacture	Aluminum rolling oils
Textile printing	Vegetable oil extraction

Properties

The unusually wide range of quality requirements demanded by the industry is met by products manufactured specially for each industry, with different boiling range, density, color, solvent strength, aromatic content, sulfur and evaporation rate. With few exceptions these are straight run products from crude oil distillation with the boiling range adjusted to the required flash point and end use. These specific cuts may be subjected to further treatment such as hydrotreating, solvent extraction, and/or acid/clay treatment to improve color, odor, taste, remove aromatics and sulfur, and make the solvent suitable for various end uses.

Color

Color of industrial naphtha or distillate is a partial indicator of its degree of refining. Typically industrial naphthas have colors ranging from water white to straw color and are measured by ASTM D156 (Saybolt color). Color of an industrial naphtha is an extremely important parameter for some end users. Thus a colored naphtha is totally unacceptable for use in dry cleaning because of its negative effect on clothes if used. For identical reasons many industrial users such as in the paint, varnish, and lacquer industries cannot compromise on naphtha color.

Volatility

Volatility of naphthas is characterized by its flash point and ASTM distillation. Flash point provides a qualitative index of fire and explosion hazard in the shipping and handling of the naphtha. Also it is required for choosing the correct shipping container, labeling, classification, and transportation of the product. An appropriate distillation range of naphtha is of immense importance for a given end use. The distillation range of naphthas is indicative of the relative evaporation rate. The distillation range of naphthas is measured by ASTM D 86. Aromatics such as benzene, toluene, or xylenes are either pure single compounds or very close boiling monomers. These have a very narrow boiling range and are measured by ASTM D 850.

Evaporation Rate

The evaporation rate is another important characteristic of petroleum solvents. It is related to volatility and is of great importance in many consuming industries such as paints, varnishes, dry cleaning, and other cleaning jobs because it provides information on the time required for any specific solvent to dry completely. Many variables are involved in the determination of evaporation rates, such as ambient temperature, relative humidity, atmospheric pressure, vapor pressure of solvent, and heat of vaporization. The test method for measurement of evaporation rates is ASTM D 3539. A thin film evaporation apparatus is used to determine the evaporation rates of volatile organic solvents. The instrument measures weight loss as a function of time under specific environmental conditions. Evaporation rates are generally reported in comparison with two organic liquids; butyl acetate and ethyl ether.

Solvency

Large volumes of industrial naphthas are used primarily as solvents. Solvency of a naphtha is a function of its composition. Naphthas are derived from diverse crudes, and naphtha composition varies greatly depending on its crude source and distillation range. Aliphatic hydrocarbons have a lower solvency compared with naphthenic and aromatic hydrocarbons. Aromatics have the highest solvency. Solvency is generally measured by the aniline Point (ASTM D 611) or Kauri-butanol (ASTM D 1133) value.

Aniline Point (ASTM D-611)

The aniline point is the minimum equilibrium solution temperature for an equal volume of aniline ($C_6H_5NH_2$) and the sample. A specified amount of aniline and the sample or aniline plus heptane and the sample are placed in a test tube, and the mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate, and the temperature at which the two phases separate is recorded as the aniline point or mixed aniline point

The aniline point or mixed aniline point is useful as an aid in the characterization of pure hydrocarbons or mixtures. Aromatic hydrocarbons exhibit the lowest values and paraffins, the highest. Naphthenes and olefins exhibit values that are between aromatics and paraffins. In a homologous series, the aniline point increases with increasing molecular weight. The aniline point is often used to provide an estimate of the aromatic hydrocarbons content of the mixture.

The mixed aniline point is determined for samples having an aniline point below the temperature at which aniline crystallizes from the mixture (20.8°F). In the test, 10 mL of aniline is mixed with 5 mL of the sample and 5 mL of heptane, and the aniline point of the mixture is determined.

Kauri-Butanol Value (ASTM D 1133)

The Kauri-butanol (Kb) value of a solvent is defined as the number of milliliters of the solvent at 20°C that can be added to 20 g of a standard 20 percent stock solution of kauri resin (polar nature) in butyl alcohol without causing cloudiness. Kauri resin is readily soluble in butyl alcohol but not in hydrocarbon solvents. The resin solution will tolerate only a certain amount of dilution. Stronger solvents such as toluene can be added in greater amounts and thus have a higher Kb value than a weaker solvent like hexane. Kauri-butanol value is a measure of solvent power of hydrocarbon solvents. A high kb value indicates relatively strong solvent power.

Aromatics

The higher the aromatic content of an industrial naphtha, the greater its solvency. Therefore the PONA (paraffin, naphthenes, olefins, and aromatic content) of naphthas is of importance in determining the suitability of the naphtha or distillate for a specific application. However, aromatics are generally known human carcinogens and so their concentration is kept to the lowest feasible level. Benzene is particularly toxic and thus undesirable in any industrial naphtha. The distillation range of naphtha is so chosen to exclude benzene, for example in food-grade hexane. Aromatics can also be eliminated by acid and clay treatment or severe hydrotreating of feed naphtha.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PCAHs) are known human carcinogens, which are present in higher boiling petroleum fractions. Any petroleum products that are likely to be used directly in pharmaceuticals, in food, or come in indirect contact with food or in animal feed such as hexane for edible oil extraction, medicinal-grade white oils, waxes, and so on, must be free from these compounds. Measurement of PCAHs concentration (more than 0.01 ppm) is done by ultraviolet (UV) absorption. Government regulations in most countries normally lay down test methods and standards for the permissible levels of PCAHs allowed in food, pharmaceuticals, and personal care products.

Solvent Toxicity

There are no completely safe solvents. Contact with liquid solvent or inhalation of vapors they emit into the air can be hazardous. Solvents can irritate and damage the skin, eyes, and respiratory tract, cause a narcotic effect on the nervous system, and can damage internal organs such as the liver and kidneys. Solvent toxicity is measured in terms of the two factors described next.

TLV-TWA. The threshold limit value is an 8-h the time-weighted average (TWA) set by the ACGIH (American Conference of Government Industrial Hygienists). The threshold limit is expressed in parts per million. TLV-C, is similar to an OSHA permissible limit (PEL), or a workplace environmental limit (WEEL), from the American Industrial Hygiene Association, is also used.

OT. OT is odor threshold, in parts per million. OT is generally stated as a range of the amount that normal people can detect. Solvents whose odor cannot be detected until the concentration is above the threshold limit are particularly hazardous. Evaporation rates, TLV, and OT values for some petroleum and organic solvents are shown later in Table 21-16.

MAJOR APPLICATIONS OF PETROLEUM SOLVENTS

n-Hexane

Hexane finds its most important use in vegetable oil extraction processes. Normal hexane is used in the extraction of peanut, soybean oil, rapeseed, sunflower seeds, cottonseed oil, castor oil, corn oil, linseed, coca beans, sugarcane, and in the production of a very large number of vegetable oils, mainly for human consumption and also for nonedible oils. It is also used in the extraction of fats and oils from wool and meat scraps. Table 21-3 lists the properties of various hexane isomers. Hexane is manufactured from a paraffinic crude. A narrow cut, typically 145 to 158°F, is separated by fractionation from light naphtha broad cut to contain most of C6 hexane isomers. This cut may also contain benzene, a known human carcinogen, which must be reduced to 500 ppm or lower.[1] Because the relative volatility of benzene is very close to that of hexane isomers, complete separation of benzene by fractionation is generally not economical without a large number of separation

TABLE 21-3 Properties of Hexane Isomers

Component	Formula	Molecular weight	Boiling point,°F	Density
n-Hexane	C_6H_{14}	86.2	155.7	0.664
2-methyl pentane	C_6H_{14}	86.2	140.5	0.658
3-methyl pentane	C_6H_{14}	86.2	145.9	0.669
2,2-dimethyl butane	C_6H_{14}	86.2	121.5	0.654
2-3-dimethyl butane	C_6H_{14}	86.2	136.4	0.666
Benzene	C_6H_6	78.1	176.2	0.884

plates. Benzene and other polynuclear aromatics are removed from the cut by one of the following processes:

- By sulfuric acid and clay treatment. Hexane cut is treated with 5 percent v/v 95 percent sulfuric acid. Acid sludge formed is separated. Hexane is treated with approximately 2 percent by weight activated clay and next filtered.
- By extraction with a solvent for aromatic separation, such as furfural, n-methyl pyrrolidone.
- By severe hydrotreating to saturate aromatics.

The properties of food-grade hexane[2] are presented in Table 21-4.

TABLE 21-4 Food-Grade Hexane

Color	Saybolt, Min.	+30
Density	68°F, Max.	0.687
Distillation		
Initial boiling point	°F, Min.	145
Dry point	°F, Max.	158
Nonvolatile residue	ppm (w/w)	10
Aromatic	Vol %, Max.	1
Saturates	Vol %, Min.	98.5
n-Hexane content	Wt %, Min.	85
Sulfur content	ppm(w/w), Max.	75
Water-soluble acid	mg/g	0.0003
Lead	g/L	0.0005
Phosphate	ppm (w/w)	20
Chlorides	(as Cl) ppmw, Max.	20
Bromine number	Max.	1
UV absorbance per cm optical path length, Max.		
210 nm		1.00
220 nm		0.20
230 nm		0.10
240 nm		0.04
250 nm		0.02
280–400 nm		0.01

Vegetables Oil Extraction

A metering bin meters the seeds into the process system. The seeds are next conveyed to a roller mill that reduces the seeds to flakes 0.012 to 0.015 in thick. The flakes are then conveyed to the dryer and brought to a temperature of 220°F at approximately 4 percent moisture content. The kernels are conditioned at 240°F and the moisture is reduced to 3 to 4 percent before entering the expeller press.

As the next step the oilseed is cleaned and dried. Foreign materials like stones, glass, and metal are taken out by sieving and magnets and disposed of. Drying is done with hot air or combustion gases using natural gas.

Preparation of the seeds before extraction depends on the kind of seeds and the required quality of the meal. Seeds with a high oil content like rapeseed and sunflower seed are usually mechanically pressed in an expeller after a preheating step in indirectly heated conditioners. The expeller cake is next further treated in the extractor. In some cases the expeller cake containing some oil is sold as such for animal feed.

Oilseeds with a low oil content such as soybean is mechanically and thermally treated and sent directly to the solvent extraction unit. Some oil seeds such as soybean and sunflower seeds may be dehulled after the cleaning step. After dehulling, the meal will have a lower crude fiber content and hence a higher protein content. The hulls can separately be used for feeding purposes as such or in pelletized form.

The preprocessed seeds (soya flakes), the expeller cake, is extracted in an extractor in a multistage countercurrent procedure with the help of a solvent (normal hexane) until the remaining oil is reduced to the lowest possible level. The hexane-containing meal is treated in a desolventizing toaster where it is heated indirectly and with steam. The desolventizing toasting process serves three purposes; to separate the solvent from the meal, to increase the nutritional value of meal by reducing the content of glucosinolates or trypsin inhibitors, and to minimize the risk of biological contamination.

To obtain a stable and transportable animal feed material that is suitable for storage, the meal is subsequently dried and cooled. The moisture content of the meal is reduced from 18 to 20 percent to less than 1.5 percent. The meal is next sent to silos for storage. In order to prevent sticking of the oil meals to the walls of the silos, an anti-caking agent (mineral clays, bleaching clay, etc.) is added. The anti-caking agents are those limited by foodstuff legislation.

The miscella, a mixture of oil and solvent, is separated by distillation into two components; oil and solvent (hexane). The solvent is recycled to the extraction process.

The use of hexane in solvent extraction has some negative features too. Even with the most efficient desolventizer/toaster units, some hexane may remain in the meal, which can run as high as 0.5 percent. The known mild toxicity of this trace contaminant in animal feed precludes the use of solvent extracted meal for a number of end uses. Also, hexane is "too efficient" a solvent; it extracts virtually every oil-soluble fraction, including up to 5 percent of unwanted but nutritionally very valuable materials, referred to as "unsaps." This means that the meal, now contaminated with hexane, no longer contains these oil-soluble critical nutrients (phytosterols, vitamin E family tocols, phosphatidyl choline, and other natural lecithins). Additional chemicals, particularly caustic soda, and severe thermal processing is required, implying higher processing costs and degrading more unsaps to sludge.

Heptane

Heptane is also a paraffinic naphtha, and it is used in place of hexane where a higher flash solvent with lower evaporation rate is required. Properties of n-heptane are shown in Table 21-5.

TABLE 21-5 Properties of n-Heptane

Mol wt	100.2
Boiling point, °F	209.2
Specific gravity	0.6882
Aniline point, °F	157.5
Kauri-butanol value, ASTM 1133	
Evaporation rate (n-Butylacetate = 1)	
Kinematic viscosity, 100°F, cSt	0.521
Research octane	0
Vapor pressure, 100°F, kPa	11.16
Heat capacity, LIQ., 1 atm Btu/lb, °F	0.5276
Heat of vaporization, Btu/lb, at normal B.P, 1 atm	135.99

Light Naphthas

Rubber Solvent. This low boiling aliphatic solvent is used in the manufacture of rubber cements and adhesives, rubber tires, brake linings, intaglio inks, leather degreasing, paints. and lacquers. Typical properties of rubber solvent are listed in Table 21-6. The boiling range is 154 to 275°F. Aromatics are generally restricted to below 5 percent by weight.

TABLE 21-6 Rubber Solvent

Specific gravity, 60°F	0.697
Distillation, ASTM	
IBP,°F	154
Dry point, Max.,°F	275
Aromatics, Wt %, Max.	5
Aniline point, °F	140
Kauri-butanol value	33 (Min.)
	45 (Max.)
Vapor pressure, kPa, 68°F	12

Lacquer Solvents. The principal use of this product is as a diluent in the preparation of lacquer and synthetic coating, where a quick drying material is required. Its evaporation rate is comparable with that of toluene, and it is frequently used in conjunction with toluene.

Varnish Makers' and Painters' (VM & P) Naphtha. It is typically a straight run naphtha cut (235 to 285°F) from crude oil. It has a flash point of 40 to 50°F. Its principal use is in thinning spray paints and for thinning oil-based enamels, alkyd paint, and varnish. It is also employed in the manufacture of rubber cements, adhesives, waxes, and polishes. It is also referred to as "light naphtha" and as "spotting naphtha." Typical properties of this naphtha are shown in Table 21-7.

TABLE 21-7 Varnish Makers' and Painters' (VM & P) Naphtha

Specific gravity, 60°F	0.758
Aromatics, Wt %	<1
Kauri-butanol value	36
Distillation range, °F	242–300
Flash point, °F	50
Evaporation rate, n-Butyl acetate = 1	2

Petroleum Distillates

Mineral Spirits. Mineral spirits, petroleum spirits, and Stoddard solvent are all different types of hydrocarbon solvents or petroleum distillates used in the coating industry and in dry cleaning. Stoddard solvent was originally developed for the dry cleaning trade. Mineral spirits find application in many other industries such as metal cleaning and degreasing.

Petroleum distillates have been the most widely used solvents in dry cleaning. At the beginning of the 20th century, gasoline was the solvent of choice; however because of the fires and explosion associated with the use of gasoline, in 1928 a new solvent called Stoddard solvent with a minimum flash point of 100°F was introduced in the United States. Stoddard solvent is a kerosene cut with a boiling range of 300 to 415 °F. Stoddard solvent remains popular to the present day. However, the flash point of the cut was raised to 140°F (Table 21-8) for enhanced safety. Also, the aromatic content was lowered to a low level (less than 4 percent) to make it less toxic.

TABLE 21-8 Stoddard Solvent

Color	+25 (Saybolt, Min.)
	25 (Pt-Co)
Specific gravity	0.787
Aromatics, Wt %	<4
Doctor test	Negative
Kauri-butanol value,	30
Distillation range, °F	370–410
Flash-point, °F	140
Evaporation rate (n-Butyl acetate = 1)	0.08

Petroleum solvents in dry cleaning face severe competition from perchloroethylene (PCE), which was introduced as a dry cleaning solvent in the 1950s. The majority of the commercial dry cleaners prefer PCE because of its nonflammability and superior cleaning ability. However, compared with petroleum solvents, PCE is expensive, and dry cleaning plants must use a solvent recovery system. Solvent recovery is not practiced in petroleum solvent based dry cleaning units, due to the low cost of petroleum solvents. Also the use of chlorinated hydrocarbons in the dry cleaning industry is being viewed with increasing concern about the possible health risks to humans and the damage to the environment due to their lower biodegradability.

Dry Cleaning Process

The dry cleaning industry consists of coin-operated machines (4- to 12-kg capacity), commercial plants (14- to 27-kg capacity), and industrial units (200- to 230-kg capacity). Coin-operated units typically use synthetic solvents. Commercial units can use either synthetic or petroleum solvents. About 50 percent of industrial-scale cleaners use petroleum solvent; another 50 percent use PCE (perchloroethylene). Other popular nonpetroleum dry cleaning solvents in use are 1,1,1 trichloroethane. Use of trichlorofluoroethane (CFC-113), once a popular solvent, is prohibited because of ozone layer depletion concerns.

For synthetic solvent cleaners, the garments are first washed in "charged" solvent, which is used solvent with a small portion of detergent for better cleaning. Next the garment is rinsed with pure solvent and sent to a dryer. The solvent is filtered, and a part of this solvent is returned to the charged solvent tank. The remaining solvent is distilled to remove oils and greases, and the distilled solvent is sent to the pure solvent tank. The solids removed from the filter are heated to remove the remaining solvent. The vapors are sent to a refrigerated condenser and separator to recover the solvent. Vapors from the dryer are also sent to a refrigerated condenser. Petroleum plants are almost identical to those using synthetic solvents except that small plants do not recover solvent vapors from various operations.

Mineral Turpentine Oil

The trade name MTO, or mineral turpentine oil, refers to a colorless petroleum solvent with a boiling range of 285 to 400°F or 260 to 400°F. It is mainly used as a solvent for textile printing, dry cleaning, metal degreasing, and insecticidal formulations.

Jute Batching Oil

Jute is a natural fiber produced mainly in India and Bangladesh and is used for the packaging industry for food grains and other agricultural produce. Jute batching oil (JBO) is used to make jute fiber pliable. It also finds a limited application as wash oil for coke oven gases in the steel industry. It is typically a straight run middle distillate (465 to 700°F) cut from paraffinic crude. Polycyclic hydrocarbon content of JBO used for food packaging and thus indirect contact with food is regulated by a UV absorption test and the pyrene content of JBO (Table 21-9).

TABLE 21-9 Jute Batching Oil

Color, ASTM, Max.	L 7.0
Flash point, °F, Min., cc	212
Distillation,	
Density, 60°F, g/mL	0.85
Kinematic viscosity, cSt, 100°F, Max.	15
Initial boiling point, °F, Min.	464
FBP, °F, Max.	700
Residue, Vol %, Max.	2
UV Absorbance Test	
Pyrene content ppm, Max.	25
Absorbance per cm optical path length in the range of UV wavelength, Max.	
280–299 nm	2.3
300–319 nm	1.2
320–359 nm	0.8
360–400 nm	0.3

Aromatic Solvents

Benzene. Benzene is the lowest boiling material in the aromatic series of naphthas. Benzene is a known human carcinogen, and therefore its use is restricted as a solvent. Its principal use is now as a raw material for the manufacture of a large number of organic chemicals such as phenol, Caprolactam, benzene hexachloride (insecticide), styrene, monochlorobenzene, and various intermediates.

Toluene. When an industrial naphtha with high solvency is required, toluene is the preferred choice. It is the solvent for heavy synthetic resins and a thinner/diluent for the coatings of synthetic resins. It is one of the major components in the preparation of lacquers. Toluene is particularly recommended for situations where fast drying is required. Nitration-grade toluene is used for the manufacture of tri-nitro-toluene (TNT) explosives, saccharin, benzaldehyde, benzoic acid, and many dyes and intermediates.

Xylene. Solvent-grade xylene is in fact a mixture of ortho, para, and meta xylene isomers, and ,like toluene, has high solvency power. It is used in many types of synthetic coatings. It has a slower evaporation rate than that of toluene. Intermediate drying rates can be met by using a blend of xylene and toluene. The properties of benzene, toluene, and xylenes are listed in Table 21-10.

TABLE 21-10 Properties of Benzene, Toluene, and Xylenes

	Molecular weight	Boiling point at 1 ATM, °F	Vapor pressure at 100°F, PS1	Specific gravity, 60°F/60°F	Kinematic viscosity, 100°F	Aniline point, °F	Heat capacity liq, 1 ATM	Heat of vaporization at normal B.P, I ATM, Btu/lb
Benzene	78.108	176.18	3.224	0.8845	0.587	<22	0.4098	169.34
Toluene (methyl benzene)	92.134	231.12	1.032	0.8719	0.5584		0.4017	156.2
Alkyl benzenes								
Ethyl benzene	106.16	277.13	0.371	0.8717	0.6428	< –22	0.4118	145.7
1,2 Dimethyl benzene (O-xylene)	106.16	291.94	0.264	0.8848	0.74	< –4	0.4418	149.1
1,3 Dimethyl benzene (M-xylene)	106.16	282.39	0.326	0.8687	0.591	–22	0.4045	147.4
1,4 dimethyl benzene (P-xylene)	106.16	281.03	0.342	0.8657	0.613	–22	0.4083	146.1

White Petroleum Distillates

Petroleum solvents are highly refined distillates with high flash points. These grades are manufactured from selected crude oils by close fractionation of middle distillates (kerosene/diesel) cut to adjust the boiling range. Aromatics and unsaturates are next removed by treatment with oleum or by severe hydrotreating. The processes used for the manufacture of white petroleum distillates are similar to those used for the manufacture of white oils. The refined petroleum distillates so produced resemble very light white oils. These are colorless, tasteless, and nearly odorless. Chemically and biologically these are inert and stable and do not support pathogenic bacterial growth.

These petroleum distillates typically have a viscosity at 100°F in the range of 1.5 to 3 cSt. The initial boiling point is high, ensuring a high flash point. Boiling range is generally narrow; C_{10} to C_{15} range hydrocarbons or 380 to 450°F. Sulfur and other odorous compounds present in the feed are almost completely removed and aromatics are reduced by processing, to below 1 wt %. Properties such as solvency (aniline point and Kauri-butanol value) and pour point are a function of the feed source.

White petroleum distillates are direct substitutes for high volatile organic compound (VOC) solvents in consumer and institutional products. They lower the VOCs in such aerosol systems as air fresheners, furniture polishes, and insecticides. Vapor pressure of these solvents is generally less than 0.1 mm Hg at 68°F and are not regulated as VOCs in consumer products. Typical properties of white petroleum solvents are listed in Table 21-11.

TABLE 21-11 White Petroleum Distillates

		1	2	3	4
Specific gravity		0.786	0.795	0.800	0.812
Kinematic viscosity	100°F, cSt	1.66	2.18	2.28	4.30
Colour, saybolt	Min.	+30	+30	+30	+30
Flash Point	COC, °F	165	210	215	260
Distillation, ASTM					
IBP	°F	375	430	450	510
FBP		460	500	545	595
Aniline point	°F	170	175	181	192
Pour point	°F	–40	–15	–0.4	25
Aromatics	Wt %	<1	<1	<1	<1

Nonaerosol use of these white distillates include the following uses. Highly refined, light, odorless hydrocarbon solvents are used as a defoamer in processing beet sugar and yeast (more than 1 ppm), in modified hop extract of beer, as a float on fermentation fluids in the manufacture of vinegar and wine, in froth flotation cleaning of vegetables, as a coating on eggshells, in pest control formulations, and as insecticide bases. For use in these applications, the hydrocarbon solvent must comply with the various regulations of food and drugs administrations of various countries. White petroleum solvents are also used in fragrance bases, nail polish removers, waterless hand cleaners, as lamp oils and liquid candles where odorless and clean burning fuel is desired, charcoal lighter fluids, automotive and furniture polishes, floor polishes, industrial cleaning solvents, dust control agents, and the manufacture of paper and board.

Aluminum Rolling Oils

Cold rolling of aluminum produces products such as household foil, packaging foil, beverage cans, and tread plates. Aluminum rolling oils are used as coolants that cool, lubricate, and clean aluminum in sheet and foil rolling in cold rolling operations. Wide coils of foil are usually annealed in an atmospheric furnace before shipping. During annealing, the rolling lubricant on the coil is vaporized or burned, but some oil may remain on the aluminum foil/sheet after rolling that may come in indirect contact with food if the foil or sheet is used for packing food and beverages. For this reason, aluminum rolling oils are expected to comply with food and drug administrations regulations of various countries. These relate mainly to color, odor, and aromatic specifications of the oil.

Aluminum rolling oils are manufactured from paraffinic or naphthenic crude. A narrow diesel cut is chosen, with a boiling range of 430 to 480°F for light duty and 535 to 590°C for heavy-duty operations. Depending on the feedstock quality and product specifications, the distilled narrow cut is next severely hydrotreated to remove sulfur completely and reduce aromatics to below 1 wt %. Important characteristics of aluminum rolling oils are as follows:

- Color and odor: The product must be colorless and odorless
- High initial boiling point (IBP) and narrow boiling range: to reduce evaporation rate and thus rolling oil consumption
- Nonstaining and noncorrosive: Removal of sulfur by the hydrotreating process ensures these characteristics. Ultra-low sulfur imparts excellent nonstaining properties to the product.
- Low aromatics: For manufacture of aluminum foil for food packaging or any other use where foil is to come in contact with food, aromatics in the oil must be reduced to below 1 percent and polynuclear aromatics in oil must pass a UV absorbance test for compliance to national standards (such as FDA 178.3620, part B: indirect food contact).
- Low viscosity: These are generally low-viscosity oils (1.5 to 4.0 cSt at 100°F).

The typical properties of aluminum rolling oils are shown in Table 21-12.

TABLE 21-12 Properties of Aluminum Rolling Oils

	1	2	3
Color, Saybolt	+30	+30	+30
Specific gravity, 60°F	0.761	0.797	0.824
Distillation range, °F	420–490	450–520	500–560
Sulfur, ppm (w/w)	<1	<5	<1
Kinematic viscosity, cSt, 104°F	1.7	2.4	3.3
Aniline point, °F	190	183	180
Flash point, °F	194	220	250
Pour point, °F	21.2	–11	–49
Aromatics, Wt %	0.1	1	0.5

Printing Ink Oils

Printing inks contain four basic components: pigments, solvent, resinous binder, and performance additives. The pigments used in printing inks include both inorganic pigments such as carbon black, titanium dioxide, and organic pigments that are generally dyes rendered insoluble by complexing with a metal ion. Most organic pigments are prepared from azo, anthraquinone, triarylmethane, and phthalocyanines dyes.

There are five main printing processes and the ink for every process has to be specifically designed. Lithography is used in magazines, books, labels, newspapers, and so on. Popularity of this method comes from its low cost and high-quality reproduction with a minimum environmental impact. Lithography and letterpress are collectively known as the paste ink processes. These processes use inks that are essentially nonvolatile at room temperature.

Flexography is used in corrugated packaging, magazines, flexible films, envelopes, and newspapers. Flexography and gravure are known as liquid ink processes that are based on volatile solvents that evaporate readily at room temperatures. Screen printing uses ink that fall in between these two groups.

The choice of vehicle (solvent plus resins) for a printing ink depends on the printing process, how the ink will be dried, and the substrate on which the image is to be printed. In lithography and letterpress, where inks are dried by absorption and oxidation, vehicles are generally a mixture of mineral oils or vegetable oils and resins. Flexographic inks, which are designed to dry quickly by evaporation, can be either water based or based on an organic solvent such as ethanol, ethyl acetate, n-propanol, or isopropanol with a wide variety of resins. Vehicles for gravure inks, which also dry by evaporation, may also contain aromatic or aliphatic hydrocarbons and ketones as solvents. Inks for screen printing use organic solvents that are less volatile than those used for flexography or gravure (higher glycol ethers and aromatic/aliphatic hydrocarbons). Additives in inks include dryers, wax, and plasticizers. UV radiation cured inks commonly based on acrylates are used in all of printing processes to varying degrees.

The manufacture of ink consists of dissolving or dispersing pigment or dyes in organic solvents or oils to produce the vehicle (varnish), mixing and dispersing the pigment or dye into the vehicle, introduction of any additive, and packaging. Table 21-13 shows the properties of printing ink oils.

TABLE 21-13 Properties of Printing Ink Solvents

	Hydrotreated light distillate	Technical white oil
Specific gravity	0.7952	0.8146
Boiling range, °F	440–465	525–570
Avg. Mol wt	199	230
Color, Saybolt	+30	+30
Flash point, °F	205	260
Aromatics, Wt %	0.8	1
Pour point	–20	+20
Cloud point	–10	+27
Heat of vaporization, Btu/lb	136	130
Specific heat	0.485	0.492
Viscosity cSt, 100°F	2.01	3.9
Vapor pressure, mm Hg, 70°F	0.05	0.01
Kauri-butanol number	26.5	22
Aniline point,°F	175	191

Halogenated Hydrocarbon Solvents

Halogenated hydrocarbon solvents are usually not flammable and have no flash point. However, some can react explosively on contact with certain metals, and heating or burning them can create highly toxic decomposition products including phosgene gas. Hazardous amount of these toxic gases can be created by working with chlorinated solvents in an enclosed environment where a pilot light is burning. Clearly, all solvents should be isolated from sources of heat, sparks, flame, and static electricity.

Carbon Tetrachloride

Carbon tetrachloride was among the first chlorinated solvent used in dry cleaning. It was commonly blended with other solvents for use as a dry cleaning solvent. Because of its high toxicity and ozone-depleting properties, use of carbon tetrachloride was phased out under the Montreal Protocol in 1996.

Trichloroethylene

Trichloroethylene was introduced as a dry cleaning solvent in 1958. It caused the bleeding of acetate dyes at temperature exceeding 75°C. Trichloroethylene was never used as a primary dry cleaning solvent. Trichloroethylene is still used as a dry side precleaning and spotting agent.

Perchloroethylene

Perchloroethylene is a member of a family of aliphatic halogenated hydrocarbons. It is a colorless volatile liquid that is essentially nonflammable and has no measurable flash point.

PCE is also known as tetrachloroethylene, or "perc," and it has been used in the industry for over 50 years. It is an effective nonflammable solvent that does not contribute to the formation of smog (ground-level ozone) or to the depletion of the stratospheric ozone. PCE is the primary solvent used in commercial and industrial dry cleaning. Since being introduced in the industry in the late 1930s, it has replaced most other solvents because of its relatively low toxicity and nonflammability. Its other major uses are as a metal cleaning and degreasing solvent and as a solvent in automotive aerosols. It is also a chemical intermediate for the production of several fluorinated compounds.

Properties of perchloroethylene are shown in Table 21-14. PCE is sold under various trade names, such as DowPer, PerSec, and Perklone.

TABLE 21-14 Perchloroethylene Properties

Synonyms	Ethylene tetrachloride, 1,1,2,2 Tetra-chloroethylene
Formula	C_2CL_4
Molecular weight	165.8
Specific gravity	1.619
Boiling point, °F	250
Boiling point, solvent-water, °F	190
Specific heat, 25°C, cal/g	0.209
Viscosity, 25°C, cP	0.84
Heat of vaporization at B.P cal/g	50.1
Vapor density (air = 1)	5.76
Flash point	None
Water solubility, g/100 g, 77°F	
H_2O in solvent	0.0105
Solvent in H_2O	0.015
Refractive index, 25°C	1.503
Surface tension Dynes/cm, 25°C	31.8
Kauri-butanol value	90

It is very stable solvent and not normally corrosive. However, in the presence of heat and moisture and other chlorinated hydrocarbons, acids can form and cause corrosion problems. The presence of other chlorinated compounds such as trichloroethane, which is widely used as a spotting agent, can also contribute to acid formation in PCE.

The popularity of PCE in the dry cleaning industry can be attributed to the following properties:

- Virtual nonflammability, which led to its wide use in decentralized dry cleaning plants.
- Its high solvency (Kb-value of 90), which dissolves out most oil, greases, and fats.
- Low viscosity (0.84 cSt at 60°F) and low surface tension (32 dynes/cm) that allow it to penetrate rapidly in fibers to dissolve soils.
- The high density of perc not only facilitates mechanical action in the wash cycle, but it also helps in the separation of solvent from water in the recovery cycle.
- Perc's high evaporation rate (1.5 compared to butyl alcohol) provides for reasonable drying times at moderate drying temperature.
- Safe to use on all common textiles, fibers, and dyes.

The textile industry uses PCE as a spotting agent for removal of spinning oils and lubricants. It is also used in wool scouring and as a solvent carrier in dyes and water repellents.

TABLE 21-15 Halogenated Hydrocarbon Solvents

Solvent	Formula	Molecular weight	Specific gravity	Vapor pressure, mm Hg, 68°F	Freezing point, °F	Boiling point, 1 ATM, °F	Water solubility, mg/L 77 °F	Kauri-butanol number	Evaporation rate, Bu O Ac = 1	Viscosity, 77°F cP
Carbon tetrachloride	CCL_4	153.82	1.594	90	–9.4	169.8	800			
Trichloroethylene	$C_2H\ CL_3$	131.39	1.5		–121	188.6		130	6.4	0.53
1,1,1 Trichloro-ethane	$C_2H_3CL_3$	133.41	1.3376		–22.72	165.2	0.13			
Perchloroethylene	C_2CL_4	166	1.623			250	0.4			

TABLE 21-16 Solvents and Their Toxicity

Solvent	TLV-TWA, ppm	Odor threshold, ppm	Evaporation rate butyl acetate = 1
Ethyl alcohol	1000	49–716	
Methyl alcohol	200	4–6000	
Propyl alcohol	200	0.03–41	
Isoamyl alcohol	100	0.03–0.07	
n-Butyl alcohol	50	0.1–11	
Kerosene	None		
n-Heptane	400	230	
VN & P naphtha	300	1–40	2
Stoddard solvent	100	1–30	0.02
n-Hexane	50	65–250	
Gasoline	300	0.3	
Ethanol amine	3	2–4	
Diethanol amine	0.46	0.27	
Ethyl benzene	100	0.1–0.6	
Xylene	100	20	0.8
Toluene	50	0.2–37	1.9
Styrene	50	0.017–2	
1,1,1 Trichloroethane	350	390	
Methylene chloride	50	160	
Trichloroethylene	50	82	6.4
Perchloroethylene	25	47	
Ethylene dichloride	10	6–185	
Carbon tetrachloride	5	140–584	
Ethyl acetate	400	6.4–50	
Methyl acetate	200	180	
Isoamyl acetate	100	0.22	
Ethylene glycol	39.4 C	0.1–40	
Diethylene glycol	50 (wheel)	UNK	
Butyl cellosolve	25	0.1	
Cellosolve	5	2.7	
Acetone	750	3.6–630	
Methyl isobutyl ketone	50	0.013	
Methyl ethyl ketone	200	2–85	
Turpentine	100	50–200	0.38
Cyclohexane	300	780	

Chemical Intermediate

PCE is used as a basic raw material in the manufacture of hydrofluorocarbon (HFC) 134, a popular alternative to chlorofluorocarbon (HCFC) 123, 124, and 125.

Automotive Aerosols

Perchloroethane has replaced 1,1,1 trichloroethane in aerosol formulations for the automotive aftermarket, particularly for brake cleaning. These formulations provide auto repair shops with highly effective, nonflammable products.

Metal Cleaning/Degreasing

Many industries, including aerospace, appliances, and automotive manufacturers, use PCE for vapor degreasing of metal parts during various production stages. Its high boiling point and resultant longer cleaning cycle are advantageous in removing difficult soils, such as waxes with high melting points. The ability of this chemical to remove water during vapor degreasing is useful to jewelry manufacturers and other metal finishers.

Miscellaneous Uses

PCE is used as an insulating fluid in some electrical transformers as a substitute for polychlorinated biphenyls (PCBs). Relatively small quantities of PCE are used in printing inks, aerosol specialty products, adhesive formulations, paper coatings, and silicones. In addition, PCE is a component of chemical maskant formulations used to protect surfaces from chemical etchants used in aerospace and other industries.

1,1,1 Trichloroethane

1,1,1 trichloroethane (TCA) was introduced as a dry cleaning solvent in the 1980s. It is particularly used in leather cleaning operations. TCA is not a very stable solvent. It is used as a precleaning and spotting agent in dry cleaning. TCA is also used for degreasing motor stator coils and other machine cleaning operations using a vapor degreaser. TCA has been classified as an ozone-depleting chemical, and its use is being discouraged in the industry.

Other Dry Cleaning Solvents

1,1,2 Trichloro-1,2,2 trifluoroethane was introduced by DuPont in 1960s under the trade name Valclene. This chlorofluorocarbon (Freon 113) is used as a dry cleaning solvent. Because the vapor pressure of Valclene is approximately 20 times that of PCE, clothes cleaned in Valclene can be dried at a lower temperature, and it was promoted as a solvent of choice for the dry cleaning of delicate fabrics. Freon 113 is one of the fluorochlorocarbons subject to the Montreal Protocol, and its use has been prohibited in most countries.

Dipropylene glycol tertiary butyl (DPTB) ether has also been used as an alternative to PCE in dry cleaning. The properties of halogenated hydrocarbon solvents are shown in Table 21-15. Solvents and their toxicities are listed in Table 21-16.

REFERENCES

1. Joint FAO/WHO Expert Committee on Food and Additives, MMR Minor. Met. Review 1998, 48B.
2. Hexane specs; Council Directive 88/384/EEC on the extraction solvent used in the production of foodstuffs.