by Alan Phenix

Generic Hydrocarbon Solvents: a Guide to Nomenclature

All of us, no doubt, have encountered and used generic hydrocarbon solvents from the hardware store or chemical supply house. But how often, as we contemplated our bottle of mineral spirits, naphtha, white spirits, petroleum spirits, turps substitute, mineral turpentine, benzine, petroleum ether, ligroin, or Stoddard Solvent, have we felt that we actually knew what was in it, and what were its properties in terms of solvent power, boiling range, evaporation rate, etc.

Although conservators are becoming increasingly accustomed to proprietary hydrocarbon solvents offered by the larger petrochemical companies – Shell, Exxon Mobil, etc. - and are seeking out particular products with quite specific properties, the traditional generic solvents still arouse some considerable uncertainty regarding composition and properties.

The vagaries of nomenclature of generic hydrocarbon solvents became painfully apparent to me during the course of early work on a book on the use of solvents in conservation which is currently in progress: the situation seemed so unclear to me that I felt it necessary, for my own understanding and peace of mind, to try to untangle some of the web of confusion concerning the identity of all of the kinds of stuff we know of as generic hydrocarbon solvents. The following article is essentially an extract of some of the content of the draft chapter in the book which is concerned with hydrocarbon solvents.

It is perhaps worth mentioning at the outset that the principal ways in which these kinds of product are distinguished are by their boiling/distillation ranges (and, by association, volatility, flash point etc.) and aromatic content; these are the key properties which we should have some idea of when using such liquids. Generally speaking, with regard to aromatic content, generic hydrocarbon solvents fall into two broad groups:

those that are essentially aliphatic (ie. composed largely of linear, branched, and/or cyclic alkanes) and free from aromatic compounds, and

those that contain low to moderate proportions of aromatics, usually less than about 25%.

The presence of a fraction of aromatic compounds in an otherwise aliphatic hydrocarbon solvent will add to its polarity and solvent power, factors which may be desirable for certain purposes, for example dissolving certain polymer resins. The presence of a significant aromatic content in a largely aliphatic hydrocarbon liquid may, however, have some less desirable consequences, such as increased odor or greater degree of harmfulness.

Traditional mineral spirits or white spirits products normally have aromatic contents in the range of about 10-25% w/w. Quite a number of hydrocarbon solvent products will have been actively 'de-aromatized' to remove or chemically convert (by hydrogenation) the aromatic constituents of the original feedstock into saturated compounds, with the result that such grades often contain very few or no aromatics.

A note about CAS Registry and EINECS Numbers

When it comes to specifying any chemical substance, a good starting point is the CAS Registry Numbers or, for Europe, the EINECS (European Inventory of Existing Commercial Chemical Substances) number, which is also sometimes called the EC Number.[1] In principle, these registries of chemical substances provide an indexed catalogue of specific chemical compounds: known chemical substances – even different individual isomers of the same substance - are identified by a unique registration number. To take xylene, for example, this substance is covered by four different CAS Registry and EINECS numbers:

	xylene: mixed, or no specific isomers	*o*-xylene	*p*-xylene	*m*-xylene
CAS Registry No.	1330-20-7	95-47-6	106-42-3	108-38-3
EC No.	215-535-7	202-422-2	203-396-5	203-576-3

Hydrocarbon solvents are just one, relatively small, group of products that are the output of petroleum refineries. Like the various fuel products derived from crude petroleum (gasoline, kerosene, fuel oil, etc.) most hydrocarbon solvents are complex mixtures rather than specific individual compounds. So the approach adopted for formal description and differentiation of petroleum refinery products was a series of generic descriptors for different refinery process streams, each with its own CAS Registry Number (and by correlation, now, EC/EINECS Number), based not on chemical composition, but on the process history and final process step. The result is that over 80 CAS Numbers exist which describe different kinds of petroleum refinery output, many of which might apply to commercial solvent products.

The essential point of relevance to solvent products is that CAS Registry Numbers for petroleum refinery products are not necessarily unique descriptors of the chemical substance: refinery products with the same or substantially similar compositions may actually have different CAS numbers; furthermore, more than one CAS Registry Number may apply to any given product. CAS Registry and EC Numbers can be helpful in providing some clarification of the composition of hydrocarbon solvents, but they should

1. A good online source for finding CAS Registry numbers is the ChemIDplus database operated by the US National Library of Medicine. See: http://chem.sis.nlm.nih.gov/chemidplus
Similarly, a database of chemical substances searchable by CAS Registry and EINECS numbers is provided by the European Chemical Substances Information System (ESIS) operated by the European Chemicals Bureau; see http://ecb.jrc.it/esis/

be treated with some caution, especially if one is using them to source information on health hazards, etc.. 'Stoddard Solvent' is a good example: Stoddard Solvent has its own CAS Registry No. 8052-41-3, but one may also encounter products called 'Stoddard Solvent' which are assigned other CAS numbers, such as 64742-88-7 which identifies it as *Solvent naphtha, petroleum, medium aliphatic*, as well as several other descriptors.

Low boiling point, low aromatics (or aromatics-free) generic hydrocarbon solvents: naphthas, petroleum spirit, petroleum benzine, ligroin, petroleum ether, and related products

The terms 'petrol' or 'gasoline' are used in the petroleum industry to describe the broad fraction of volatile hydrocarbons that are distilled from crude oil between 30 and 210°C; but from this very broad fraction a whole variety of sub-fractions can be isolated and/or are marketed as solvents. At the lower end of this boiling range we find liquids that would come under the broad designation of **naphtha** or **petroleum spirits**. These two somewhat over-arching terms correctly describe some of the more volatile liquid fractions of petroleum: naphtha normally applies to refined or partly refined products of distillation of crude oil boiling in the range of approximately 40 to 100°C, or possibly a little higher to around 120°C.

Having said this, however, the term naphtha does, somewhat confusingly, also get used in the names of some petroleum-derived products that have boiling ranges sometimes quite considerably higher than 120°C, as we shall see below. There is a general convention, then, to call the products that consist of, or contain, an abundance of, lighter, lower boiling point (< ca. 140°C) compounds **'light naphthas'**, and to refer to the higher boiling point (> ca. 160°C), more dense products as **'heavy naphthas'**. Some laboratory suppliers may also offer other, higher boiling point, petroleum solvent products with specified boiling ranges under such names as 'Petroleum, Special bp 180-200°C', and while these might be largely aliphatic in composition, the CAS/EC Registry numbers applied to such products (eg. 64742-82-1) suggest these are of the 'white sprits-type' and therefore might contain up to about 20-25% aromatics.

In British usage, the term **petroleum spirits** describes very similar products to those covered by the term naphtha when applied to the more volatile products boiling below 120°C: petroleum spirit finds use commonly among the suppliers of laboratory chemicals to describe, usually, aliphatic (non-aromatic) hydrocarbon solvents within a similar range of boiling points. The English term 'petroleum spirits,' then probably equates best with the German **'Siedegrenzenbenzine'** which term is also usually accompanied with a designation of boiling range. Whilst falling within the rather broad group of products that would come under the general classification of naphtha or petroleum spirits, the very lightest, most volatile liquid hydrocarbon solvents that can be bought from laboratory chemical suppliers may also be offered under the name **petroleum ether**, (the term 'ether' signifying extreme lightness and volatility), normally with a descriptive suffix giving the boiling range.

Thus, from the leading international laboratory chemicals suppliers it is possible to buy various petroleum ethers with boiling ranges such as 30-50°C, 40-60°C, 50-70°C, 60-80°C, etc. Similar, essentially aliphatic, solvents with specific boiling ranges above 100°C are also available, but these would normally be called, at least in the UK, petroleum spirit, followed by the relevant boiling range, 100-120°C, etc. However, in the United States, laboratory grade aliphatic hydrocarbon solvents with boiling ranges as high as 100-140°C still appear to be called petroleum ether, rather than petroleum spirit. The petroleum ethers will consist mostly of mixed aliphatic hydrocarbons comprising up to about 6 or 7 carbon atoms.

Importantly, some forms of petroleum ether, like other grades of hydrocarbon solvent, are specifically identified as having been 'hydrogen-treated,' which generally means they have been hydrogenated to convert any unsaturated and/or aromatic components to saturated forms; as a rule hydrogen-treated solvents are low in aromatics and other unsaturated compounds. It should be emphasised that the petroleum ethers are extremely volatile, have very low flash points (well below 0°C), and present a significant fire hazard. Petroleum ethers will have similar properties to some of the special (low) boiling point solvents (SBPs) with comparable boiling ranges produced by several of the major petrochemical companies.

Another class of products also available from laboratory chemical suppliers are **ligroins**, which again can be considered as a sub-set of the group of naphthas/petroleum spirits. The term 'ligroin,' again often followed by a specific boiling range, applies to hydrocarbon liquids obtained by fractional distillation of petroleum typically having boiling points between about 60-110°C. Products under the name ligroin can have boiling ranges as low as 60-80°C and may be practically indistinguishable from a petroleum ether with the same boiling range. Ligroin is assigned the CAS Registry Number 8032-32-4, which is also applied to many other products, particularly the lower boiling ones, called petroleum spirit, petroleum ether, and petroleum benzine. To all intents and purposes **petroleum benzine** appears synonymous with petroleum spirit. 'Naphtha' has the CAS Registry Number 8030-30-6, which also covers petroleum benzine and petroleum ether: that is, the lower boiling point non-aromatic hydrocarbon solvents. Applied to solvents, the terms 'naphtha' and 'benzine' appear essentially synonymous in North American usage. To take a familiar example, the US laboratory chemicals supplier Fisher Scientific offers a product 'Benzine (Petroleum Naphtha)' which is commonly used by conservators. This product is identified by the CAS Registry No. 64742-89-8 which defines the product as *Solvent naphtha (petroleum), light aliphatic*. The boiling range is quoted as 118.5 – 140.5°C, and it is described as consisting substantially of aliphatic hydrocarbons, of which octane and *n*-heptane make up 1.5% and 1.2% respectively;

aromatic-content is very low, less than about 0.2%. As if to demonstrate perfectly the overlap in the names of these generic hydrocarbon solvents, Fisher's 'Benzine (Petroleum Naphtha)' conforms to the specification for a low-aromatics VM&P Naphtha (see below); indeed this is probably a re-labelled VM&P Naphtha from one of the major US petrochemical companies.[2]

On the whole, the term 'naphtha' is the broadest of all the terms which describe petroleum distillation and refinery products, and apart from the very specific instance of **VM&P Naphtha** (Varnish Makers & Painters' Naphtha), it is perhaps best to avoid this term when referring to solvents.

Higher boiling point generic hydrocarbon solvents: mineral spirits, white spirits, Stoddard Solvent, testbenzin etc.

The various solvents that we know by the common or commercial names above are some of the most difficult to describe and to distinguish. They are probably some of the most widely and frequently used solvents in conservation, but there is often considerable uncertainty in our field, and others, about their identity and composition. This is especially significant since products from this group may vary quite significantly in the magnitude of the health hazard which they present, mostly on account of their aromatic content or other possibly harmful constituents. These solvents are also quite commonly used in operations that involve, in the order of things, relatively large quantities of liquid (applying coatings such as varnishes by brush or spray, dry-cleaning, consolidation etc.), so that potential for actual exposure may be correspondingly increased. But it is not just conservation that uses the various types of white or mineral spirits in quantity: in terms of volume these solvents are probably the most abundantly used around the world.

World Health Organization (WHO) 'White Spirit (Stoddard Solvent): health and safety guide,' 1996

The world-wide health risks associated with the use of white spirits were perceived to be of such magnitude that this product was examined in depth by the World Health Organization (WHO) which published its findings in 1996. The 1996 WHO report and its associated 'Health Criteria' are an excellent starting point for consideration of the general nature and identity of solvents of the type called white spirit or mineral spirits. [1, 2] Many of the observations made in relation to white spirits apply also to the other generic distillation products discussed earlier. However, since the WHO report was published, some significant changes in the specifications of white/mineral spirits and related products have occurred, especially in North America, and it should not now be considered as an absolutely perfect reflection of the current situation.

[2] Compare, for example, the properties of Fisher 'Benzine (Petroleum Naphtha)' with Marathon Petroleum's VM&P Naphtha in Table 3.

On the basis of the situation in manufacturing before 1996, products coming under the umbrella of the terms mineral spirits or white spirits were described in the WHO report essentially as follows:

White spirit is a clear colorless solvent with very low water solubility and a characteristic odor (odor threshold: 0.5-5 mg/m^3). It is a petrochemical solvent containing mainly C_7 to C_{12} or C_{13} aliphatic, alicyclic, and aromatic hydrocarbons with a boiling range of 130-220°C. Different varieties exist which are defined according to different kinds of treatment (hydro- desulphurization, solvent extraction and hydrogenation) that the products have undergone or according to their boiling ranges or flash-points. The content of white spirit can vary, because of differences in the raw material (crude oil) and in the production processes. The different kinds of white spirit are defined, therefore, according to physico-chemical properties rather than exact chemical composition.

Different white spirit products were classified into four main types according to their production process:

Type 1: Naphtha (petroleum), hydrodesulphurized heavy. A complex combination of hydrocarbons obtained from a catalytic hydrodesulfurization process. It consists of hydrocarbons having carbon numbers predominantly in the 7-12 range and boiling in the range of approximately 90 to 230°C (194 to 446°F). Aromatics < 25% by weight; Benzene < 0.1% by weight.

Type 2: Naphtha (petroleum), solvent-refined heavy. A complex combination of hydrocarbons obtained as the raffinate from a solvent extraction process. It consists predominantly of aliphatic hydrocarbons having carbon numbers predominantly in the 7-12 range and boiling in the range of approximately 90 to 230°C (194 to 446°F). Aromatics < 5 % by weight; Benzene< 0.02 % by weight.

Type 3: Naphtha (petroleum), hydrotreated heavy. A complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst. It consists of hydrocarbons having carbon numbers predominantly in the 6-13 range and boiling in the range of approximately 65 to 230°C (149 to 446°F). Aromatics < 1% by weight; Benzene< 0.002% by weight.

Type 0: 'Straight-run' white spirit.
A distillation fraction subjected to no further treatment beyond distillation, consisting predominantly of saturated C_9-C_{12} hydrocarbons with a boiling range of 140-220°C.

Relevant CAS registry numbers are:

8052-41-3 (Stoddard solvent);
64742-82-1 (white spirit type 1);
64741-92-0 (white spirit type 2);
64742-48-9 (white spirit type 3);
64742-88-7 (white spirit type 0).

The naphtha and kerosene fractions from crude petroleum are first subjected to hydrodesulphurization, followed by fractional distillation into the appropriate boiling ranges. In the case of type 3 white spirit, hydrogenation (treatment with hydrogen over a catalyst, also termed hydrotreatment) is carried out on the fraction of hydrodesulphurized white spirit. The sequence of fractionation and hydrogenation may be reversed. Hydrogenation converts the unsaturated aromatics into saturated cycloalkanes. Consequently, hydrogenated white spirit contains straight- and branched-chain aliphatics (n- and iso-alkanes), a relatively large fraction of cycloalkanes (naphthenes), and practically no aromatics. White spirit that has not been treated beyond the process of distillation is termed straight-run white spirit (type 0).

Each of the four types may occur in three different grades: **low flash** grade (flash point: 21-30°C; initial boiling point: 130-144°C), **regular grade** (flash point: 31-54°C; initial boiling point: 145-174°C), and **high flash** grade (flash point: ≥ 55°C; initial boiling point: 175-200°C). The grade is determined by the crude oil used as the starting material and the conditions of distillation.

The most common variety of white spirit is a mixture of saturated aliphatic and alicyclic C_7-C_{12} hydrocarbons with a content of 15-20% (by weight) of aromatic C_7-C_{12} hydrocarbons and a boiling range of 130-230°C. The C_9-C_{11} hydrocarbons (aliphatics, alicyclics, and aromatics) are most abundant, constituting ≥ 80% (by weight) of the total. This ordinary white spirit is designated white spirit, type 1, regular grade, as three different types and three different grades exist. A USA variety of type 1 is called Stoddard Solvent and is a hydrodesulphurized solvent petroleum distillate defined according to its boiling range of 149-204°C and the absence of rancid or objectionable odors.

Here we see one of several different definitions of 'Stoddard Solvent.' It is of interest here to note that the WHO regarded it as a particular form of Type 1 white spirit; that is, one which contains up to 25% aromatics.

National and International Standards for hydrocarbon solvents

Various national standards which give specifications for mineral spirits solvents are summarized in Table 1. The International Standard ISO 1250: *Mineral solvent for paints - white spirits and related hydrocarbon solvents* was withdrawn in 1985 and no longer applies. That standard was, however, technically identical to the British Standard BS 245:1976 which is still in force and which gives two specifications of white spirit, with low (< 25%) and high (25-50%) aromatic contents respectively.[3]

There is a series of German DIN standards for hydrocarbon solvent products. White spirit is covered in DIN 51632 which is in two parts, each part defining one of two broad classes of white spirit. DIN 51632–1 [4] covers regular white spirit (testbenzine), which is defined as a "refined gasoline fraction with a minimum flash point of 21°C and a distillation range of 130°C to 220°C;" DIN 51632–2 [5], describes low aromatics white spirits, that is "refined gasoline fraction with a low aromatics content, a minimum flash point of 21°C, and a distillation range of 130°C to 270°C." The aromatics content of regular white spirits falling within DIN 51632–1 is not actually specified, but to comply with the standard products must contain less than 0.1% benzene by weight. Within the broad class of regular white spirit, DIN 51632 - 1 defines four separate sub-types, each having different distillation ranges: Type 1, 130 – 185°C; Type 2, 140 – 200°C; Type 3, 150 – 190°C, and Type 4, 180 – 220°C. According to the standard, a regular (N) white spirits of type 2 would be designated 'White Spirit DIN 51632 – N – 2.'

In the specification for low aromatics white spirit, DIN 51632 – 2, six separate sub-types (1-6) are defined, again according to distillation ranges: Type 1,130 - 185°C; Type 2, 140 - 200°C; Type 3, 150 - 190°C; Type 4, 180 – 220°C; Type 5, 190 - 250°C, and Type 6, 220 - 270°C. All of these sub-types are specified to have less than1% w/w aromatics, and for types 1-3 the maximum benzene content is set at 0.1%w/w. According to the standard, a low aromatic (E) white spirits of type 2 would be designated 'White Spirit DIN 51632 – E – 2'.

In addition to the above DIN standards for white spirits, some other hydrocarbon solvent products are specified under German standards. DIN 51630 [6] provides for Petroleum Spirit (also called here Spezialbenzine - Petrolether) which is described as "a special boiling-point spirit commonly used in laboratory applications, having high volatility and low aromatics content." DIN 51631[7] covers Special-Boiling-Point Spirit (also called Spezialbenzine - Siedegrenzenbenzine) which is described as a "fraction of petroleum naphtha having a narrow distillation range and a flash point below 21°C, specially treated for particular applications." Special-Boiling-Point Spirit according to DIN 51631 is classified into three types: type 1, 2, and 3. (see Table 4.7) A further type of Spezialbenzine is specified in DIN 51635 [8] which applies to FAM Standard Mineral Spirits (FAM-Normalbenzin): this is a low-boiling point product.

An Australian standard for white spirits exists in the form of AS 3530-1988. [9]

United States standards for generic hydrocarbon solvents

The ASTM standard for mineral spirit that is outlined in Table 1 has undergone considerable revision since it was introduced in 1983 as ASTM D235-83. The current, active version of that standard, ASTM D235-02: *Mineral Spirits and Stoddard Solvent,* [10], came into force in 2002, and it now stands as one of three operational ASTM standards for hydrocarbon solvents, the other two being ASTM D3735-02: *VM&P Naphthas* [11], and ASTM D3734-05: *High Flash Naphthas*. [12] These standards provide an excellent framework for understanding the nature, properties, and range of products that are presently available under these respective generic names.

Table 1. Selected standard specifications pertaining to hydrocarbon solvents

Country	Product and specification reference	Distillation: IBP / FBP[a]	Flash Point	Aromatic content (% v/v) and other compositional specs.
Germany	DIN 51630 Petroleum Spirit (Spezialbenzine – Petrolether)	IBP above 25°C FBP up to 80°C	None specified	Benzene < 0.1% w/w *n*-hexane <5% w/w
Germany	DIN 51631 Special-Boiling-Point Spirit (Spezialbenzine - Siedegrenzenbenzine)	Type 1 60 min. - 95°C max. Type 2 80 min. - 110°C max. Type 3 100 min. - 140°C max.		Benzene < 0.1% w/w *n*-hexane <5% w/w Aromatics: Type 1 <0.1% Type 2 <0.2% Type 3 <0.2%
Germany	DIN 51632 – 1 Regular white spirit (Testbenzine)	Overall, 130 – 220°C Four separate sub-types specified: Type 1 130 - 185°C Type 2 140 - 200°C Type 3 150 - 190°C Type 4 180 – 220°C	Overall, 21°C min Type 1 21°C min Type 2 21°C min Type 3 35°C min Type 4 55°C min	Not specified (benzene < 0.1 g/100g ≡ 0.1% w/w)
Germany	DIN 51632- 2 Low aromatics white spirit (Testbenzine)	Overall, 130 –270°C Six separate types (1-6) specified: Type 1 130 - 185°C Type 2 140 - 200°C Type 3 150 - 190°C Type 4 180 – 220°C Type 5 190 - 250°C Type 6 220 - 270°C	Overall, 21°C min Type 1 21°C Type 2 21°C Type 3 35°C min Type 4 55°C min Type 5 65°C min Type 6 65°C min	Max 1% w/w aromatics Benzene < 0.1% w/w Benzene < 0.1% w/w Benzene < 0.1% w/w - - -
Germany	DIN 51635 FAM standard mineral spirit (FAM-Normalbenzin)	60 - 95°C 85-95% distilled by 90°C		Benzene < 0.1% w/w *n*-hexane <5% w/w Aniline point 59-61
UK	(BS 245: 1976) Mineral solvent (white spirit, type A)	<1% below 130°C; <10% below 145°C; <90% below 200°C; end point not above 220°C	above 32°C	< 25%
UK	BS 245: 1976 Mineral solvent (white spirit, type B)	<1% below 130°C; <10% below 145°C; <90% below 200°C; end point not above 220°C	above 32°C	25-50%
International Standard	Mineral solvent for paints - white spirits and related hydrocarbon solvents. (ISO 1250). Withdrawn 05.01.85	(technically identical to BS 245: 1976)		
Australia	White Spirit [c] AS 3530 - 1988	IBP 145°C min – 155°C max 10% recovered 150°C min – 160°C max 50% recovered 160°C min – 170°C max 95% recovered 180°C min – 190°C max FBP 200°C	31°C	-
USA	(ASTM D235-83)[b] (now obsolete) Mineral spirit type 1 - regular (Stoddard solvent)	149 °C min - 208°C max	38 °C min	-

Notes:

[a] IBP = initial boiling point; FBP = final boiling point

[b] Also includes specifications for high flash-point (60 °C min), odourless (Kauri-butanol value, 29 max) and low dry-point (185 max). This standard now superseded: current specification is D235-02

[c] The Australian standards for mineral turpentine and white spirit are almost identical, the only real difference being in the Aniline Point values (mineral turpentine : 20-25°C) and (white spirit : 50-56°C) which suggests that 'mineral turpentine', in Australian usage, is higher in aromatics than white spirit.

Generic Hydrocarbon Solvents: a Guide to Nomenclature, continued

ASTM D235-02 Standard Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent)

ASTM D235-02 goes some way to clarifying the descriptive terminology of hydrocarbon solvents. By its own description "this specification covers four types of hydrocarbon solvents, normally petroleum distillates, used primarily in the coatings and dry-cleaning industries. 'Mineral Spirits' is the most common name for these solvents. They are also called 'Stoddard Solvents' when used for dry cleaning."

It is of interest to note that, at least in the eyes of ASTM, the name 'Stoddard Solvent' might be applied to any of the solvents specified in ASTM D235-02.

ASTM D235-02 defines four distinct types of mineral spirits:

Type I - Full Range.
Type II - High Flash Point.
Type III - Odorless.
Type IV - Low Dry Point
(ie. low final boiling/distillation point).

Each of these four types of Mineral Spirits is then further differentiated according to aromatics content as follows:

Class A - 8 to 22 vol % aromatics.
Class B - 2 to 8 max vol % aromatics.
Class C - less than 2 vol % aromatics.

An exception are the 'Odorless' grades (Type III): being inherently low in aromatics, these only exist in Class C forms. For Type III 'Odorless' solvents, two separate Class C types are specified, C-1 and C-2, which are similar save for the fact that C-2 has a higher Bromine Number and therefore higher olefinic content.

Table 2. Physical and chemical properties of different types of Mineral Spirits according to ASTM D235-02

		Type I Full Range Mineral Spirits			Type II High Flash Point			Type III Odorless [B]		Type IV Low Dry Point		
		Class A	Class B[A]	Class C[A]	Class A	Class B[A]	Class C[A]	C-1 [A]	Class C-2 [A]	Class A	Class B[A]	Class C[A]
Aromatic Content, range, vol %		8–22	2–8 max	0–2	8-22	2-8 max	0-2	0–0.25	0–0.25	8-22	2-8 max	0-2
Commercial reference		regular	rule 66	low aromatic	regular	rule 66	low aromatic	odorless	odorless	regular	rule 66	low aromatic
Appearance		clear and free of suspended matter when observed at 15-25°C										
Flash point, (°C),		38	38	38	61	61	61	38	38	38	38	38
Color,		Min. not darker than + 25 on Saybolt Scale										
Kauri-Butanol value	*min*	34	29	28	33	29	28	….	….	34	29	28
	max	43	40	39	43	40	39	29	29	43	41	40
Bromine Number, max		5	1	0.1	5	1	0.1	0.1	5	5	1	0.1
Distillation, (°C)												
Initial boiling point, min		149	149	149	177	177	177	149	149	149	149	149
50 % Recovered, max		185	185	185	202	202	202	196	196	174	174	174
Dry point, max		213	213	213	213	213	213	213	213	185	185	185
Residue from distillation: Vol %, max		1.5										
Acidity		neutral										
Apparent Specific Gravity (15.6/15.6°C)	*min*	0.754	0.754	0.754	0.768	0.768	0.768	0.740	0.740	0.754	0.754	0.754
	max	0.820	0.810	0.800	0.820	0.810	0.810	0.775	0.775	0.810	0.800	0.790

Notes:
A. Mineral Spirits of Types I, II, III, and IV may be commercially available as Classes B and C to meet certain air pollution regulations (for example, "Rule 66") which set maximum limits on certain constituents as follows:
toluene and ethylbenzene 20 vol %, C8 and higher aromatics 8 vol %, olefins 5 vol %; the sum of all restricted constituents not to exceed 20 vol %.
B. Only products that have a very high isoparaffinic hydrocarbon content, that is, approaching 100 %, are considered to fit the odorless category. Type III Class C-1 is a hydrogenated product; Class C-2 is a distillation fraction.

In summary, ASTM D235-02 specifies different types of mineral spirits which are designated as follows:

Type IA Regular Mineral Spirits, 8-22% aromatics; Stoddard Solvent

Type IB Mineral Spirits, 2-8% aromatics, Rule 66; Stoddard Solvent

Type IC Mineral Spirits, 0-2% aromatics; Stoddard Solvent

Type IIA Mineral Spirits, High Flash, 8-22% aromatics; Stoddard Solvent

Type IIB Mineral Spirits, High Flash, 2-8% aromatics, Rule 66; Stoddard Solvent

Type IIC Mineral Spirits, High Flash, 0-2% aromatics; Stoddard Solvent

Type III Mineral Spirits, Odorless

Type IVA Mineral Spirits, Low Dry Point, 8-22% aromatics; Stoddard Solvent

Type IVB Mineral Spirits, Low Dry Point, 2-8% aromatics, Rule 66; Stoddard Solvent

Type IVC Mineral Spirits, Low Dry Point, 0-2% aromatics; Stoddard Solvent.

Key physical and chemical properties of these various types of mineral spirits are summarized in Table 2 which is an abridged version of what is presented in the Standard document itself. Some solvent manufacturers indicate in their technical literature, where appropriate, compliance of particular products with any of the ASTM D-235 mineral spirits types.

ASTM 3735-02 Standard Specification for VM&P Naphthas

In similar fashion to the specification for mineral spirits described above, ASTM 3735-02 "covers four types of moderately volatile hydrocarbon solvents, mainly aliphatic in composition and normally petroleum distillates. These solvents are used primarily by the coatings industry and are commonly referred to as VM&P naphthas." 'VM&P Naphtha,' then, is generally understood to describe hydrocarbon solvents similar to mineral spirits, but which are somewhat more volatile, having boiling points mostly in the range 120-145°C. The low-aromatics types have much in common with the higher boiling products called 'petroleum spirits' described earlier.

ASTM 3735-02 defines four types of VM&P naphtha the physical and chemical properties of which are shown in Table 3:

Type I - Regular.
Type II - High flash.
Type III - Odorless.
Type IV - Low aromatics

VM&P Naphtha types I and II generally contain a moderate amount of aromatics (<20%), while Types III and IV, by their nature, are very low in aromatics, less than 1% and 2% respectively. Most of the products supplied today under the name VM&P naphtha are generally of the low aromatics or odourless types. Shell Chemicals presently only produces one product under the general name VM&P Naphtha, namely VM&P Naphtha HT, and the properties of this solvent are included in Table 3 for comparison with the specifications in ASTM D3735. However, until quite recently Shell produced several products with this designation: in the 1990s four different grades of VM&P Naphtha were produced by Shell. Again, the properties of these now obsolete grades are included in Table 3 for comparison purposes. It should be noted that the current Shell product VM&P Naphtha HT has a much narrower, and slightly higher, boiling range than the similarly-named product that was available in 1997.

A note about Rule 66

It will be noticed that, like CITGO's Special Naphtholite 66/3, quite a number of solvent products offered by US suppliers include in their names the designation '66' or 'Rule 66,' as does the ASTM D 235 classification of mineral spirits (see Tables 2 and 3). This designation serves to indicate compliance with the California's air pollution control Rule 66 which seeks to regulate emissions of photochemically active volatile organic compounds into the atmosphere.[3] The rule is particularly aimed at commercial or industrial processes which may liberate solvent vapours directly or else combustion products of solvents; and while Rule 66 may not be of immediate relevance to small-scale processes as generally apply in conservation - since the limits for organic emissions are way in excess of what a conservator would normally be using – the rule is significant with regard to specification of solvent composition. For hydrocarbon solvents Rule 66 has a bearing on olefinic and aromatic content. 'Rule 66' hydrocarbon solvents, therefore, are those with olefinic contents of less than 5% and, more pertinently, ≥ C8 aromatic contents of less than 8%. According to ASTM D235-02, 'Rule 66' solvents are those with aromatics contents between 2 and 8%: solvents with aromatics less than 2% are classed as 'low aromatic.'

Stoddard Solvent

It is perhaps appropriate to end this discussion of generic hydrocarbon solvent names with arguably the most indeterminate of the lot: 'Stoddard Solvent.' Not only can the term Stoddard Solvent be applied to products having quite different compositions and properties, but it would appear also that the meaning of the term is understood somewhat differently at least, for example, between the United States and the UK. The reader is advised, therefore, to approach and to use the term Stoddard Solvent with some caution: alone, without further qualification, it may not be a very precise descriptor of any given hydrocarbon solvent product.

An obvious starting point for identifying the chemical nature of Stoddard Solvent is the CAS Registry listing. Stoddard Solvent has its own specific entry under CAS Registry Number 8052-41-3 (corresponding to EC/EINECS No. 232-489-3) which identifies the substance as *'Low boiling point naphtha – unspecified, Stoddard Solvent.'*

[3] The full text of Rule 66 can be found, for example, at www.arb.ca.gov.drdb/sd/curhtml/r66.htm

Table 3. Physical and chemical properties of different types of VM&P naphthas according to ASTM 3735-02

	ASTM 3735-02 Specification				Selected Commercial Products						
					Current in 2006	Obsolete				Current in 2006	
	Type I [A]	Type II [A]	Type III [B]	Type IV	^Shell VM&P Naphtha HT (Typical) CAS 64742-89-8	^^Shell VM&P Naphtha HT ** 1997 Spec.	^^Shell Super VM&P Naphtha 1997 Spec.	^^Shell VM&P Naphtha EC*** 1997 Spec.	^^Shell High Flash VM&P Naphtha 1997 Spec.	Marathon Petroleum VM&P Naphtha CAS 64742-89-8	Citgo Special Naphthalite 66/3 = ASTM D3735 Type IV VM&P
Commercial reference	regular	high flash	odorless	low aromatic							
Appearance	clear and free of suspended matter and undissolved water.										
yBromine number, max	5	5	5	5							
Color	not darker than + 28 on the Saybolt scale, or 10 on the platinum-cobalt scale.				+30	+30	+30	+30	+30		
Aromatics, volume %, max	20	20	1	2	0.2	<0.4	12	7.0	11	<1	0.2
Distillation, (°C)											
Initial boiling point, min	113	138	113	113	131	119	122	121	150	119	130
50 % recovered, max	135	160	135	135	-	125	126	124	161		
Dry point, max	54	177	154	154	144	139	135	134	173	141	142
Flash point, min (°C)	4	23	4	4	20	12.8	11.1	14	34	10	19
Kauri-butanol value min	30	30	...	30	36	35	43	38	39	32	36
Kauri-butanol value max	45	45	30	38							
Apparent specific gravity, (15.6/15.6°C) min	0.715	0.715	0.715	0.715	0.761	0.746	0.761	0.754	0.774	0.744	0.762
Apparent specific gravity, (15.6/15.6°C) max	0.792	0.792	0.760	0.760							
Apparent specific gravity, (25/25°C) min	0.709	0.709	0.709	0.709							
Apparent specific gravity, (25/25°C) max	0.786	0.786	0.754	0.754							

Notes

A. Type I and Type II may be commercially available to meet certain air pollution regulations that limit C8 and higher aromatics to not more than 8 volume %, total aromatics to not more than 20 volume %, olefins to not more than 5 volume %, and total aromatic plus olefins to not more than 20 volume %.

B. Only products that have a very high isoparaffinic hydrocarbon content, that is, approaching 100 %, are considered to fit the “odorless” category.

^ from Shell Datasheet 2006

^^ from Shell product datasheet 1997

** VM&P Naphtha HT is a medium evaporating hydrocarbon solvent. It has an increased cycloparaffin content and hence solvency. The high degree of general refining gives this solvent its low level of impurities such as sulphur, olefins, benzene and total aromatics and low odour.

*** VM&P Naphtha EC is a medium evaporating solvent which contains 7% Xylene. High cycloparaffin content gives it a slightly higher solvency than similar products with the same aromatic content.

However, insight into North American usage of 'Stoddard Solvent' is given in ASTM D-235 for mineral spirits. As already mentioned above, any of the kinds of mineral spirits covered by ASTM D-235 may also be called Stoddard Solvent when they are used for the purpose of dry-cleaning. (The name Stoddard derives from the name of the inventor of the dry-cleaning process.) Accordingly, by that general definition, 'Stoddard Solvent' could apply to any of a number of products ranging, for example, from more volatile products (the 'Full Range' or 'Low Dry Point' types), possibly with up to 22% aromatics, to odorless or low-aromatics (<2%) types with final boiling points well above 200 °C, and vice versa.

'Stoddard Solvent,' however, appears to be comprehended differently in Europe. In the UK the connection with dry cleaning is often not made: 'Stoddard Solvent' seems more to be understood as laboratory grade white spirits, which may simply reflect the manner in which products called 'Stoddard Solvent' actually reach the small-scale consumer, typically via a laboratory chemicals supplier. Stoddard Solvent from the UK division of VWR International is said to comply both with ASTM D235 Mineral Spirits Type 1 and the British Standard for white spirit BSS 245. 1976: Type A. This appears to tie in with the definition of Stoddard Solvent by the WHO, noted earlier, as a variety of Type 1 white spirit.

A toxicological profile for Stoddard Solvent is the subject of a report by the US Department of Public Health & Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), and this document adds some qualifications to the identification of Stoddard Solvent simply as 'mineral spirits used for dry-cleaning' and helps to distinguish Stoddard Solvent, at least as understood in North America, from some other generic hydrocarbon solvents such as benzine, naphtha, and mineral spirits. [13] Broadly speaking, the report summarizes that "Stoddard Solvent may be considered a subset of mineral spirits."

A final note, the area of proprietary solvents is a huge subject, which will be dealt with at length in the forthcoming book. However, I wanted to give at least a few examples of some familiar solvents. During the 1990s Shell (Americas) offered quite a number of products based on generic names, such as Mineral Spirits or VM&P Naphtha, but just two products retaining these names remain in the current Shell (Americas) product range: VM&P Naphtha HT and Shellsol OMS (Odorless Mineral Spirits). Information on composition and properties of these two solvents is provided here, together with data on two other proprietary Shell solvents which are quite commonly used in conservation.

Table 4. Properties of some selected current Shell (Americas) hydrocarbon solvents. Shell Chemicals now classifies all the various hydrocarbon solvent products it offers worldwide into the following categories:
Isoparaffins;
Aliphatic mineral spirits (from fast-evaporating to high flash point mineral spirits);
White spirits/mineral spirits blends;
Special (low) boiling point solvents (SBPs); and
Aromatics and high aromatic blends.

Shell Chemicals classification		Special Boiling Point Solvents	Isoparaffinic Hydrocarbons	White Spirits / Mineral Spirits Blends	Aliphatic Mineral Spirits
Product name		**VM&P Naphtha HT**	**Shellsol OMS (Odorless Mineral Spirits)**	**Shellsol 7 EC**	**Shellsol D38**
CAS No.		64742-89-8	64741-65-7	-	64742-88-7
Property	*Unit*				
Distillation, IBP	°C	131	175	160	159
Distillation, DP	°C	144	200	202	181
Relative Evaporation Rate (nBuAc=1)	-	1.0	0.1	0.15	0.21
Composition					
Paraffins	% V	33	96	57	42
Naphthenes (cycloparaffins)	% V	67	4	36	57
Aromatics	%	0.2%	<0.1%	7	<0.2%
Benzene		<0.0002%	<1ppm	<1ppm	<0.5ppm
Flash Point	°C	20	51	43	41
Kauri-Butanol Value	-	36	29	35	34
Aniline Point	°C	60	84	63	66
Hildebrand Solubility Parameter	(cal/cm_)-	7.7	7.4	7.6	7.9
Hydrogen Bonding Index	-	-	0	0.4	-
Fractional Polarity	-	-	0	0	-

References

1. White Spirit (Stoddard Solvent): health and safety guide. (Health and safety guide no. 103). United Nations Environment Programme, International Labour Organisation. World Health Organization, Geneva 1996. ISBN 92 4 151103 6.

2. White Spirit (Stoddard Solvent) Environmental Health Criteria 187. United Nations Environment Programme, International Labour Organisation. World Health Organization. International Programme On Chemical Safety. Geneva. 1996. ISBN 92 4 157187 X.

3. British Standard BS 245:1976. Specification for mineral solvents (white spirit and related hydrocarbon solvents) for paints and other purposes.

4. DIN 51632-1 Regular white spirit - requirements and testing (Supersedes DIN 51632, 1988).

5. DIN 51632-2 Low aromatics white spirit - Requirements and testing (Supersedes DIN 51632, 1988).

6. DIN 51630 Petroleum Spirit (Spezialbenzine – Petrolether).

7. DIN 51631 Special-Boiling-Point Spirit (Spezialbenzine - Siedegrenzenbenzine) (Supersedes 1988 edition).

8. DIN 51635 FAM standard mineral spirit (FAM-Normalbenzin) (Supersedes 1981 edition).

9. Australian Standard AS 3530-1988. Solvents - Mineral turpentine and white spirit.

10. D235-02 Standard Specification for Mineral Spirits (Petroleum Spirits) (Hydrocarbon Dry Cleaning Solvent).

11. D3735-02 Standard Specification for VM&P Naphthas.

12. D3734-05 Standard Specification for High-Flash Aromatic Naphthas.

13. Toxicological Profile For Stoddard Solvent. US Department of Public Health & Human Services, Agency for Toxic Substances and Disease Registry, June 1995.

A Further Note

Ah, what's in a name...

Adding to the aforementioned complications in nomenclature, there is also the “formerly known as” problem.

In a recent conversation, Scott Blair, of Conservation Support Systems, said that in the 20 years he has been in business, Shell has changed the names of some of its solvents 3 or 4 times. Most recently, designations were changed to reflect flash points, except, of course, when they don't, as in the case of SHELLSOLS A-100, 15, and 7 EC, where they indicate aromatic content.

As we go to press, here are a few name changes that might help.

Cyclo Sol 53 became Cyclo Sol 100 which became **SHELLSOL A 100**

SHELLSOL 71 became **SHELLSOL OMS**

SHELLSOL 140 HT became SHELLSOL 142 HT became **SHELLSOL D 60**

SHELLSOL 340 HT became **SHELLSOL D 38**

Shell MS 135 became **SHELLSOL 15**

Shell MS 145EC became **SHELLSOL 7 EC**

Shell MS 146 HT became **SHELLSOL D 40**

(And then depending on which data sheet you see, it can be either SHELLSOL or ShellSol. Personally, I prefer the latter, but apparently they are using the all caps version lately.)

TS 28, actually a cocktail of solvents, was discontinued. Scott now offers CSS 28 which is made from the original Shell recipe.

Also, Scott has two convenient cocktails, made at the prompting of Jill Whitten and Rob Proctor, which are mineral spirits with a higher aromatic content:

CSS-30 Solvent 30% aromatic

CSS-50 Solvent 50% aromatic.

Carolyn Tallent