SPRAY TECHNOLOGY & MARKETING

Specialty Petroleum Hydrocarbon Fluids

Solutions Today for Tomorrow's Aerosols

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Introduction—History of Petroleum Hydrocarbon Solvents

Petroleum hydrocarbon solvents have come a long way since Colonel Drake drilled that first well in western Pennsylvania in 1859. Originally, refiners would simply distill crude oil into fractions for different uses and applications, including solvents. Pennsylvania Grade crude oil is sweet (low sulfur), with relatively low aromatics and relatively low odor, so it does not require extensive processing. This approach for producing hydrocarbon solvents worked well for many years, but over time, there arose a need for better quality specialty fluids.

These early hydrocarbon solvents were composed of four types of constituents: (1) saturated hydrocarbons such as normal paraffins, isoparaffins, cycloparaffins (naphthenes), (2) aromatics, for example, one ring aromatics such as toluene or two ring aromatics such as naphthalene, (3) olefins and (4) polars, for example, compounds containing sulfur, nitrogen or oxygen. Solvents derived directly from crude oil were a mixture of all four types and contained up to 25% aromatics.

Today's specialty petroleum hydrocarbon fluids are composed almost entirely of saturated hydrocarbons. Several factors have been instrumental in the evolution of hydrocarbon solvents into specialty petroleum hydrocarbon fluids, including advancements in processing technology, increasingly demanding application requirements, and more stringent health, safety and environmental regulations.

Evolution of Specialty Petroleum Hydrocarbon Fluids

Process technology improvements have allowed tailoring hydrocarbon fluids for specific applications. Improved fractionation has led to narrow boiling range products that provide consistent evaporation rates and controlled, higher flash points. Hydrotreating, which saturates aromatic compounds into cycloparaffins, has made the fluids non-hazardous and some fluids even pass FDA requirements for indirect or direct food contact. These specialty fluids are generally water-white with no or only faint hydrocarbon odors. Other technology advancements have led to the physical removal or the isomerization of normal paraffins so that the resulting fluids have very low pour points.

The two most important hydrocarbon fluid criteria are the boiling range and

Table 1:
A Partial Menu of Specialty Petroleum Hydrocarbon Fluids for the Formulator

	Conosol C-145	Conosol C-170	Conosol C-200	Drakesol 205	Conosol 215	Conosol 260
Boiling Range, °F	380-465	390-500	455-530	435-485	450-520	520-615
K-B Value	34.0	32.0	29.0	26.5	26.9	23.8
Aniline, °F	160	165	172	175	175	187
Aromatics, wt%	<0.5	<0.5	<0.5	<1	<0.5	<0.5
Flash Pt, °F	152	176	210	205	212	250
Pour Pt, °F	-70	<-57	<-40	-20	-40	-40
Saybolt Color	+30	+30	+30	+30	+30	+30
Vis. 40°C, cSt	1.5	1.9	2.3	1.94	2.0	4.2
VOC, ARB 310, wt%	60	30	0	0	0	0
Predominant Composition	Naphthenic	Naphthenic	Naphthenic	Paraffinic	Isoparaffinic	Isoparaffinic

the chemical composition. The boiling range determines the evaporation rate, molecular weight, flash point and viscosity of the fluid. The chemical composition determines the solvency, purity, pour point and stability of the fluid. It is the distillation range and relative ratio of the normal paraffins to isoparaffins and cycloparaffins which give the various specialty hydrocarbon fluids their unique properties.

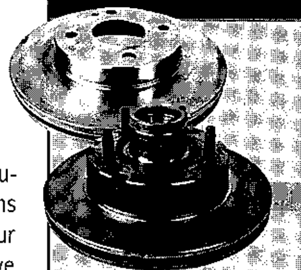
There are pros and cons to the three saturated hydrocarbon structures. Normal paraffins have high oxidation stability, but high pour points and low solvency. Cycloparaffins have high relative solvency, but slightly lower oxidation stability. Isoparaffins have high oxidation stability, low pour points, but low solvency. A mixture of all three chemical structures balances the properties. In applications where solvency is paramount, a fluid rich in cycloparaffins would be the product of choice. If low pour points were critical and solvency was not an issue, then a fluid rich in isoparaffins would be preferred. The formulator has the ability to pick and choose from multiple fluids to meet the technical requirements of stability, pour point, solvency, evaporation rate, etc.

The distillation range of the fluid is often paramount for the formulator. For our discussions, specialty petroleum hydrocarbon fluids encompass the distillation range of 350 to 650°F. Many specialty fluids have extremely narrow distillation ranges. The difference between the initial boiling point and the end boiling point by ASTM D 86 is often 50 to 75°F. These narrow fractions provide product consistency and reliable, repeatable evaporation rates. In many formulations, the solvent is designed to evaporate at a controlled rate. Narrow boiling fractions provide that control to the formulator. Conversely, some formulations require that the solvent not readily evaporate.

The fractionation process can be tailored to ensure that the more volatile constituents are removed from the fluid and do not end up in the formulation. Narrow distillation ranges as well as proper fractionation can have a positive impact on the formulation. For example, in a residual insecticide formulation, the solvent needs to evaporate fairly rapidly so that only the active insecticide is on the surface. However, with an engine degreaser, the solvent needs to remain in contact with the surface so that the actives can clean the parts. Examples are provided later in this article.

The solvency of the fluid is determined by the chemical composition. Solvency is generally characterized by the Kauri-Butanol Value (K-B Value) or by the Aniline Point. The higher the K-B Value or the lower the Aniline Point, the greater the solvency. Hydrocarbons with ring structures lead to higher solvency. Thus, fluids with high cycloparaffin or aromatic content have higher solvency than fluids rich in high normal or isoparaffinic structures. Aromatics have been associated with adverse health effects so cycloparaffins provide the highest solvency and highest safety. However, in many applications, aromatics are necessary when an aggressive solvent is required. Many active ingredients, such as insecticide ingredients, are polar compounds that require fluids with greater solvency, such as the cycloparaffins, to ensure dissolution.

Example 1:
VOC Compliant Brake Part Cleaner Formulation



	Non-Compliant	Compliant
Odorless Mineral Sprits	10.00	—
Methyl Alcohol	3.50	—
Hexane	80.00	21.00
Acetone	—	35.00
Conosol C-145 (Penreco)	—	37.50
Carbon Dioxide Propellant	6.50	6.50
Total	100.00	100.00
VOC Content	93.5%	43.5% *

* CARB VOC Standard is 45%, effective December 31, 2002.

Regulatory Impacts

The most significant factors that have driven the evolution of generic hydrocarbon solvents to specialty hydrocarbon fluids are more stringent health and environmental regulations. California Rule 66 (aka Rule 102) was one of the first regulations to push toward better air quality and lower hazardous air pollutants. This rule drove the reduction of aromatics in solvents and led to advanced processing referred to earlier. California Proposition 65 for improved water quality provided similar impetus. Banning of Ozone Depleting Chemicals (Montreal Protocol) led to increased usage of hydrocarbon propellants in aerosols, which while compatible with hydrocarbon fluids, added to air quality woes because of added Volatile Organic Compounds (VOCs).

Of course, the most significant driver has been federal and state VOC regulations, especially for consumer products; these have caused the greatest difficulties for the aerosol formulator. California (plus several other states) and the EPA have mandated significant reduction of VOCs in consumer products, many of them aerosols, as shown in the CARB website at www.arb.ca.gov/consprod/regs/cpreg.pdf.

The Formulator's Challenge

Most, if not all, aerosol products have been or will need to be reformulated to replace non-compliant mineral spirits and other volatile chemicals with VOC exempt constituents such as the low vapor pressure specialty petroleum hydrocarbon fluids (LVP VOCs). The formulator will still have some flexibility in trade-off of product attributes, as shown in Table 1, which shows a range of properties for several LVP VOC products of different chemical composition. Several excellent examples of reformulated products can be found in recent articles by Ian Gecker of Ian Gecker and Associates.[1,2,3] Hydrocarbon fluids shown in these examples have a range of VOC exemptions, allowing the formulator to reduce the VOC content of the formulations to below government-mandated levels. These formularies for household and automotive aerosol products require the solvent to remove contaminants, dry in an acceptable time period, and not leave a noticeable residue. Hydrocarbon fluids with high cycloparaffinic content, narrow boiling range, and relatively low boiling points meet these needs.

Example 1 is for a brake part cleaner which has been reformulated to reduce the high VOC content. The formulator's dilemma is to maintain solvency (K-B Value) and drying time while meeting the regulatory requirement to reduce the VOC content to below 45%. The acetone is 100% VOC exempt and the Conosol C-145 is 40% VOC exempt (60% VOC content). The total VOC content of the formulation is 21% + (0.60 X 37.50%) = 43.5 wt%. This is below the CARB VOC Standard of 45% that becomes effective December 31, 2002.

In Example 2, a combination of specialty petroleum hydrocarbon fluids is used to replace the deodorized kerosene in an engine degreaser. The combination of ingredients allows the formulator to meet the competing requirements of solvency, evaporation rate and VOC content. The Conosol C-200 and the nonylphenol ethoxylate are both VOC exempt. All the other ingredients are 100% VOC. The total VOC content of the formulation is 5% + 20% + 10% = 35%. This meets the CARB VOC Standard of 35% that becomes effective December 31, 2004.

Specialty petroleum hydrocarbon fluids can be used with normal propellants used in aerosols, such as compressed gases or hydrocarbons, which allows the formulator additional flexibility in conjunction with the specialty petroleum hydrocarbon fluid.

How About Gelled Aerosols?

The future of specialty hydrocarbon fluids is not stagnant. There have been significant strides in terms of purity and functionality over the decades. But new technologies are constantly being developed to respond to the ever-changing regulatory environment. For example, there are specialty petroleum hydrocarbon fluids now available from Penreco that have been gelled to provide viscous matrices. Fine particles can remain suspended indefinitely in high viscosity gelled fluids. These gelled fluids maintain their high viscosity so that active ingredients dissolved or suspended in the fluid can adhere to a vertical surface. The potential use of gelled specialty fluids in aerosols is just one example of the continual evolution of the industry.

Conclusion

This whole evolutionary process has created a need for the formulator to work closely with hydrocarbon fluid suppliers to identify the appropriate solvent for each application. New technologies and ways to apply them will evolve from this type of joint collaboration. Your specialty hydrocarbon supplier, who knows your market, can help navigate the ever-changing regulations and manage the logistics associated with supplying fluids in diverse geographical areas.

References

[1] Gecker, Ian R., "Lowering VOC Levels, Reformulating Household Products," *Spray Technology*, p. 28, July, 2001.

[2] Gecker, Ian R., "Lowering VOC Levels, Reformulating Automotive Products," *Spray Technology*, p. 20, November, 2001.

[3] Gecker, Ian R., "Lowering VOC Levels, Reformulating Industrial Products," *Spray Technology*, March 2002. [This article appears in this issue of *Spray Technology*—Ed.]

Example 2:
VOC Compliant Engine Degreaser
(Solvent Type/Hose Off)

	Non-Compliant	Compliant
Deodorized Kerosene	80.00	—
Ethylene Glycol Butyl Ether	5.00	5.00
Conosol 130 (Penreco)	—	20.00
Conosol C-200 (Penreco)	—	60.00
Nonylphenol Ethoxylate (4-5 mole)	5.00	5.00
Aeron A-108 (Diversified CPC International)	10.00	10.00
Total	100.00	100.00
VOC Content	95%	35% **

** CARB VOC Standard is 35%, effective December 31, 2004.