KETONES

Acetone, MEK, MIBK, DIBK, and DAA

Shell Chemicals

KETONES ARE STRONG POLAR SOLVENTS AND ARE USED IN A VARIETY OF APPLICATIONS INCLUDING:

- Paints and coatings (major end use)
- Adhesives
- Magnetic tape
- Inks
- Cleaning
- Aerospace
- Extraction

IF YOU WANT TO KNOW WHERE WE CAN TAKE YOU, LOOK AT WHERE WE'VE BEEN

From the beginning, Shell chemical companies have built a reputation for a broad product range, technical expertise and manufacturing excellence. We are one of the largest petrochemical concerns in the world with manufacturing facilities in 13 countries and marketing hubs in 3 global regions with customer service covering 55 countries.

We draw on more than 80 years of experience in the solvents business and provide assistance to customers regarding solvent selection, solvent regulations and general HSSE support. It is this commitment and customer focus that allow us to remain an industry leader.

We have been producing solvents for the marketplace since the 1920s and are continually developing new, innovative products. We are committed to being leading-edge suppliers in today's global marketplace.

Although Shell Chemicals have continued to develop new solvent alternatives, we have maintained our commitment to our core solvent products, including hydrocarbon solvents, alcohols, glycol ethers and ketone solvents. Shell pioneered the use of ketone solvents, has manufacturing sites in Europe, and is a major global supplier. Shell maintains an excellent global supply position to satisfy anticipated demand for the ketone family of solvents. Figure 1 gives the typical properties for the ketones available from Shell Chemicals, including acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), di-isobutyl ketone (DIBK) and diacetone alcohol (DAA).

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FIGURE 1

Typical properties of Shell Chemicals ketone solvents.

	DMK Acetone	MEK Methyl Ethyl Ketone	Methyl Isobutyl Ketone	DIBK Di-isobutyl Ketone	DAA Diacetone Alcohol
Molecular weight	58	72	100	142	116
Specific gravity (apparent)					
15.6/15.6°C (60/60°F)	0.7967	0.8105	0.8050	0.8124	0.9431
20/20°C (68/68°F)	0.7925	0.8065	0.8014	0.8095	0.9397
25/25°C (77/77°F)	0.7879	0.8023	0.7976	0.8064	0.9361
Density, kg/l (lb/gal)					
15.6°C (60°F)	0.796 (6.64)	0.810 (6.76)	0.804 (6.71)	0.812 (6.77)	0.942 (7.86)
20°C (68°F)	0.791 (6.60)	0.805 (6.72)	0.800 (6.68)	0.808 (6.74)	0.938 (7.83)
25°C (77°F)	0.786 (6.56)	0.800 (6.67)	0.795 (6.64)	0.804 (6.71)	0.933 (7.79)
Boiling point, °C (°F)	56 (133)	80 (176)	116 (241)	168 (334)	168 (334)
Vapour pressure @ 20°C, kPa	25	9.5	1.9	0.16	0.12
Freezing point, °C	-95	-86	-85	-42	-43
Refractive index @ 20°C	1.359	1.379	1.396	1.413	1.421
Heat of vapourisation @ T_{boil}, KJ/Kg	525	433	364	277	377
Specific heat (liquid) @ 25°C, cal/g	0.51	0.51	0.53	0.51	0.45
Flash point, Tag closed cup, °C (°F)	-18 (0)	-6 (21)	15 (59)	50 (122)	60 (140)
Flammable limits in air, %v/v					
Upper Limit	13	11.5	8.0	6.2	6.9
Lower Limit	2.1	1.8	1.3	0.8	1.8
Solubility @20°C, %wt					
Solvent in water	complete	25	2.0	0.05	complete
Water in solvent	complete	12	2.4	0.45	complete
Azeotrope with water					
Solvent content, %wt	none	88.7	75.7	49.0	12.7
Boiling Point, °C (°F)	–	73.4 (164)	87.9 (190)	97.3 (207)	99 (210)
Viscosity, mPa.s					
@ 20°C	0.32	0.42	0.62	0.92	3.4
@ 25°C	0.31	0.40	0.59	0.86	2.9
@ 30°C	0.30	0.38	0.56	0.80	2.4
Surface Tension @20°C, mN/m (=dyn/cm)	24	25	24	23	30
Solubility Parameters					
Hildebrand (HSP), $(cal/cm^3)^{1/2}$	10.0	9.3	8.4	7.8	9.2
Hydrogen Bonding Index (HBI)	12.5	10.5	10.5	9.8	6.5
Fractional Polarity	0.695	0.510	0.315	0.123	0.312

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SHELL KETONES CAN MEET THE CONTINUING CHALLENGE OF FORMULATING LOWER VOC SYSTEMS

Many regulations designed to reduce urban ozone levels restrict the emissions of volatile organic compounds (VOCs) which can react to form ozone. Coatings and adhesive formulators, as well as other solvent users, must meet guidelines and regulations for VOC emissions, while maintaining finished product quality and minimising costs. Shell ketones offer several advantages in meeting these challenges.

Because of its low ozone-producing photochemical reactivity, acetone is not considered a VOC in most air quality regulations. Other ketones have lower densities compared to esters with similar evaporation rates, as shown in Figure 2. Many VOC regulations, as well as those of state and local agencies, establish the allowed weight of VOC that can be contained in a given volume of the finished product. Both the lower density and the higher solvent strength of ketones assist formulators in producing economical, high-quality, high-solids formulations that comply with these regulations. Higher solvent strength leads to the lower viscosities of ketone solutions compared to esters, as illustrated in Figure 3, for an adhesive system. Because DAA has two functional groups, it has exceptional solvent strength for such a slow-evaporating solvent, which means less solvent may be required. As regulations evolve over time and the amounts of solvent permitted are reduced, formulators are under continuous pressure to reduce solvent levels, which means continuing advantages for ketone solvent use.

The slower-evaporating ketones (e.g. MIBK and particularly DAA) can help reduce VOC emissions in applications such as wipe cleaning. Because of their low volatility, less of these solvents are used. Thus, VOC emissions are lowered in applications where the solvent is exposed to the atmosphere during use. For example, the vapour pressures of MIBK (14.5 mm Hg) and DAA (0.9 mm Hg) are well below the 45 mm Hg maximum for wipe cleaning in the US federal aerospace regulation.

FIGURE 2

Comparison of densities (Kg/litre) of ketones and esters at 15.6°C.

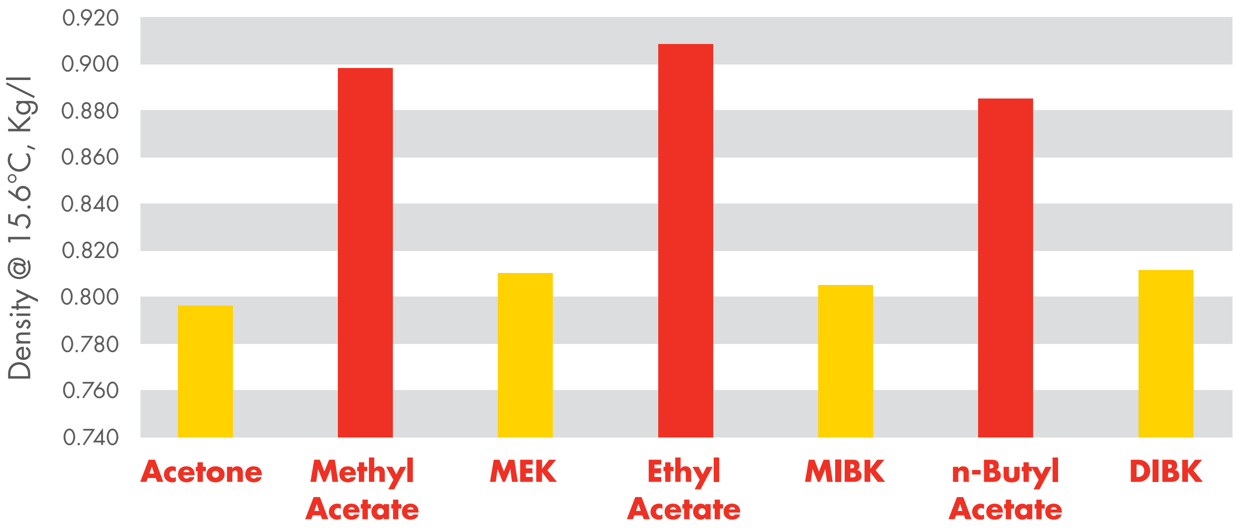
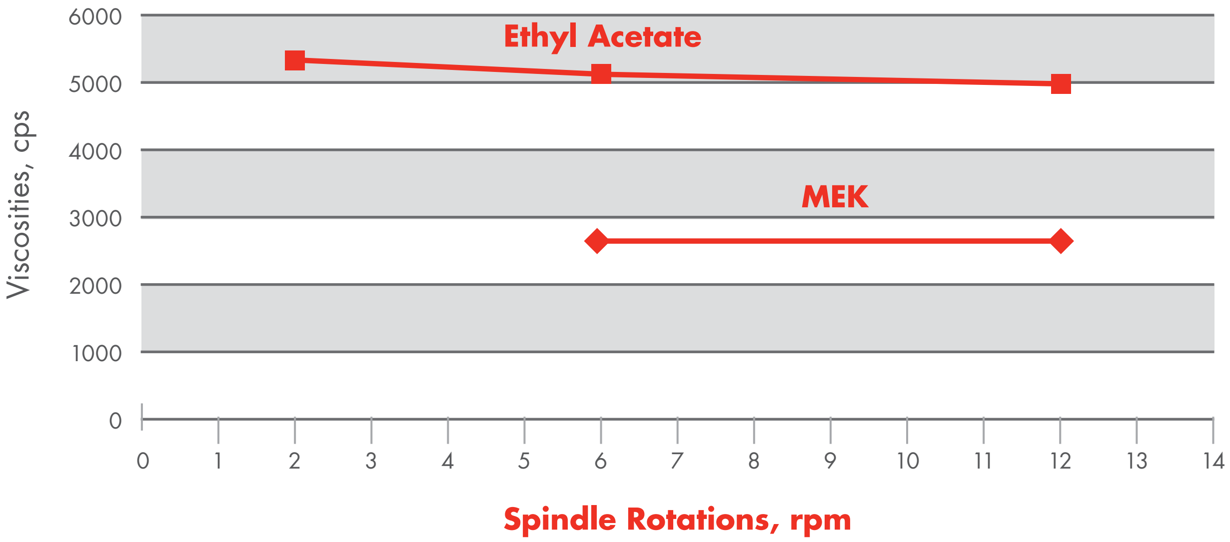


FIGURE 3

Comparison of low-shear Brookfield viscosities of adhesive solutions in ketones and esters.



KETONES BENEFIT FORMULATION OF LOWER-VOC, HIGHER-SOLIDS PAINTS AND COATINGS

The VOC limits for paints and coatings present the formulator with the task of developing high-solids coatings, which are easy to apply and form high-quality films. To achieve proper performance with these coatings, the formulator must not only work with lower molecular weight polymers or resins, but also exercise great discretion in solvent selection. Choosing the correct solvents contributes much to high-performance, high-solids (low solvent) coatings and helps keep costs in line.

It is important to note that most regulations specifically limit the maximum weight of solvent for a given volume of coating. Since viscosity reduction is generally proportional to the volume of solvent, the higher volume per pound for ketones means greater solvent reduction.

In addition to lower density, ketones have higher solvent power than esters. Thus at the same composition, ketones can dissolve more resins. For the high-solids coatings prompted by VOC regulations, ketones' higher solvent strengths lead to lower viscosities than esters. In a poorer solvent, resins tend to curl. In a solvent with a greater affinity for that resin, however, the resin molecules will tend to elongate. In low-solids coatings, the resin molecules are dilute enough to remain separate, so the coiled resin molecules will have a lower viscosity than the elongated molecules in the stronger solvent. In high-solids coatings, however, the resin molecules in the poorer solvent will tend to associate with other resin molecules to form tangled groups, which effectively increases the molecule size, giving higher viscosities. The effects of solvent strength on resin shape in low- and high-solids coatings are contrasted in Figure 4.

For high-solids systems, the combined effects of ketones' lower density and higher solvent strength compared to those of ester solvents are illustrated in Figures 5 and 6. Figure 5 compares viscosities at constant weight % solvent for several resins, and Figure 6 compares the required solvent content for the same viscosity. These benefits not only help formulators meet ever tightening VOC limits, but also provide cost savings.

FIGURE 4

Different effects of solvent strength on resin molecule shape in dilute versus high-solids systems lead to lower viscosities in high-solids systems for resins dissolved in ketones compared to resins dissolved in lower-strength esters.

High-Solids Solutions	**Dilute Solutions**
Good solvent, lower viscosity	Good solvent, higher viscosity
Poor solvent, higher viscosity	Poor solvent, lower viscosity

FIGURE 5

Viscosities (in cP @ 25°C) show ketones provide lower viscosity than esters at equal solvent concentrations in higher solids solutions of 350g of solvent per litre of solution.

	Fast Evaporating		**Medium Evaporating**	
	MEK	Ethyl Acetate	MIBK	n-Butyl Acetate
Long oil alkyd[1]	9.9	13.5	16.5	24
Epoxy resin[2]	6.9	13.0	13.5	23
EPONEX† Resin 1510	4.9	7.9	9	13
Acrylics[3]	300	510	530	750

[1] Beckosol 10-024

[2] EPON† Resin 828

[3] Acryloid® AT-400 – A product of Rohm & Haas Co., supplied at 79% wt. solids in methyl n-amyl ketoneand diluted to concentration with solvent indicated.

FIGURE 6

Grammes of ketones and esters per litre of solution required to give equal viscosities.

	Fast Evaporating			Medium Evaporating		
	Viscosity (CP @ 25°C)	MEK	Ethyl Acetate	Viscosity (CP @ 25°C)	MIBK	n-Butyl Acetate
Long oil alkyd[1]	27	250	286	51	250	278
Epoxy resin[2]	33	250	290	74	250	265
EPONEX† Resin 1510	18	250	289	29	250	284
Acrylics[3]	300	350	378	530	350	370

[1] Beckosol 10-024

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BENEFITS OF KETONES EXTEND TO WATER-BASED APPLICATIONS

Ketones are more soluble in water than esters with similar evaporation rates. For MEK and ethyl acetate, this difference is almost an order of magnitude, 27% compared to 2.9%. For MIBK and n-butyl acetate, the water solubilities are both low. However, MIBK is more water-soluble at 2% compared to <1% for n-butyl acetate. DAA is unique in that it is multifunctional, having both a ketone and hydroxyl group. Thus DAA has significantly higher solvent strength than a solvent with similar evaporation time and only one functional group. Because of the additional hydroxyl group, DAA is completely miscible with water. The ketone group makes DAA an excellent solvent for polar resins. This combination makes DAA a unique solvent for water-based coatings. Ketones are also less reactive than resins when in contact with water, which means water-based systems using ketones will have a longer shelf life.

KETONE SOLVENTS PROVIDE A VARIETY OF COST-SAVING BENEFITS

For several reasons, ketones are cheaper to use than esters, even if the cost per unit is the same. Since ketones have lower densities for each unit of mass you get more volume, and therefore a greater dilution effect. Because of the ketones higher solvent strength, less solvent is required to dissolve a resin than with esters.

Another benefit of the higher solvent strength of ketones is their ability to combine with low-cost hydrocarbon solvents to give solvent blends as effective as pure esters. For example, the following solvent systems give the same viscosity in nitrocellulose lacquers: 70% MEK + 30% toluene = 100% ethyl acetate; 80% MIBK + 20% toluene = 100% n-butyl acetate. Figure 7 contains additional data comparing viscosities of several resin solutions dissolved in esters, compared to those dissolved in mixtures of ketones and aromatic hydrocarbons.

The ability to use more hydrocarbons and still dissolve a set amount of resin is further demonstrated by the data in Figure 8. In these data the resin is first dissolved in the oxygenated solvent (ester or ketone) at a 50% weight solution. This solution is then combined with an aliphatic hydrocarbon solvent at 75:25, 40:60, 54:66 and 100:100 ratios. The ability of the solvent blend to dissolve the resin is recorded as completely dissolved (clear solution), cloudy solution, separated into two liquid phases, or resin solid precipitates out. The polyurethane is not soluble at 50% with resin in the straight ester, but is soluble in pure ketone, but even when diluted with up to 66% hydrocarbon, which clearly demonstrates the higher solvent strength of ketones.

FIGURE 7

Viscosities of resin solutions dissolved in esters compared to resin dissolved in mixtures of ketones and hydrocarbon solvents, including aromatic hydrocarbons

Blend Composition, %w						Resin Solution Viscosities @ 20°C, in cP		
EtAc	MEK	NBu Ac	MIBK	Toluene	Xylene	NC[1]	Acrylic[2]	Epoxy[3]
100						44	25	486
	70			30		27	21	331
		100				92	47	1230
			80		20	55	35	885

[1] Nitrocellulose E400 (15% w solids)

[2] Acrylic Qulester Q173 (50% w solids)

[3] Epoxy Epicote 1107 (50% w solids) N.S. = Non-solvent blend for this resin

FIGURE 8

Effects of hydrocarbon dilution on the solvency of resins dissolved in ketones versus esters.

Resin	% HCS added	Resin (% w)	Ethyl Acetate SBP* 80/95	MEK SBP* 80-95	n-Butyl Acetate SBP* 100/140	MIBK SBP* 100/140
Polyurethane[1]	25	40	–	++++	–	++++
	40	35	–	++++	–	++++
	66	30	–	++++	–	++++
	100	25	–	+++	–	+++
Polyvinylacetate A[2]	25	40	++	++++	+	+
	40	35	++	++	+	+
	66	30	++	++	+	+
	100	25	+	+	+	+
Polyvinylacetate B[3]	25	40	++	++++	++	++
	40	35	++	++	+	++
	66	30	++	++	+	+
	100	25	++	++	+	+
Polyamidoamine[4]	25	40	++++	++++	++++	++++
	40	35	++++	++++	+++	++++
	66	30	+++	++++	++	++++
	100	25	++	++++	++	++++

++++	Clear solution
+++	Cloudy solution
++	Two phases
+	Resin precipitates

[1] Neorez U314

[2] Mowilith 20 HM2279

[3] Vinnapas B5 HM2278

* SBP = Aliphatic hydrocarbons with specified distillation ranges (80-95°C and 100-140°C)

KETONES OFFER GREATER STABILITY OVER A RANGE OF CONDITIONS

At high temperatures as well as in alkaline and acidic conditions, esters tend to hydrolyse into their parent acids and alcohols. Ketones, because of their chemical nature, do not hydrolyse. Figure 9 gives the analysis in terms of acid number for MEK, MIBK, ethyl acetate and n-butyl acetate. Analysis was performed on fresh product, product stored at 50°C for 13 weeks, product stored in contact with water at 50°C for 13 weeks and product boiled at azeotropic conditions for 120 hours. The acid numbers (mg KOH/100g) for the esters are approximately an order of magnitude higher for all of the aged samples, clearly demonstrating the higher stability of ketones.

SHELL KETONE SOLVENTS

Like Shell, ketones have been important elements in the solvent industry for decades. The properties of high solvency and excellent stability made ketones the solvent of choice for coatings and many other applications such as adhesives, inks and cleaning. Changes in the marketplace, particularly regulations on VOC content, have created new requirements that give ketones an additional advantage in many systems. Acetone is not considered a VOC by most regulations. Both the lower density and higher solvency of ketones compared to the corresponding ester alternatives contribute to a reduction in VOC content just by switching to ketone solvents such as MEK and MIBK. Because of its dual functionality, DAA has high solvent strength, slow evaporation rate, and complete solubility in water, which gives DAA unique advantages as a solvent in water-based coatings systems.

FIGURE 9

Relative stability of ketones and esters at several aging conditions in terms of acid number (mg KOH/100g measured by modified ASTM D1613).

Aging Conditions/ Acid Number	MEK	Ethyl Acetate	MIBK	n-Butyl Acetate
Fresh product	2.0	3.4	1.5	6.1
13 weeks at 50°C	4.7	23.5	4.2	7.1
13 weeks at 50°C with water	2.1	20.7	2.3	19.0
120 hours boiling azeotrope	27.3	218	4.3	1250

For further information on Shell Ketone Solvents or any other Shell Chemicals product, including product technical data sheets, Safety Data Sheets, and contact information, please visit our website at www.shell.com/chemicals .