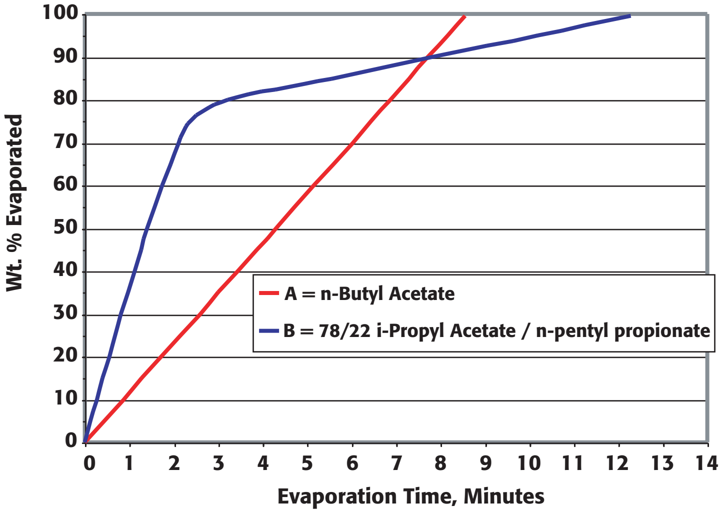
The Search for Exxate Fluids Replacements for
Solventborne Coatings

Since ExxonMobil Chemical Co. announced the discontinuation of its Exxate™[1] fluids line, users of these solvents have been seeking suitable replacements. Although specified in a variety of applications, Exxate fluids have found frequent use in solventborne coatings. Coatings manufacturers who need to replace these products in their formulations can be faced with a multi-step process that is demanding in terms of time and effort, and often costly. Most will begin the process by developing a list of potential replacements. The very lucky ones will find a drop-in replacement that functions as a direct substitute, but even these formulations require lab testing and validation. In many cases, no direct replacement is found, and the product requires complete reformulation, with all of the time and testing it takes to achieve performance that is equal to or better than the original formulation.

Figure 1/Evaporation profile of n-butyl acetate compared to i-propyl acetate/n-pentyl propionate blend



In addition to matching performance characteristics, a new formulation must also meet regulatory requirements, such as HAPs and TSCA. Certainly no manufacturer wants to introduce a new product that contains more VOCs than the old one! Next, is the new product as durable as the old one? Can it pass storage and shelf-life testing? How about environmental conditions and application methods? If the new formulation has successfully cleared these hurdles, the next step is to win customers' acceptance. For OEM and military applications, this often means an additional level of even more stringent testing, frequently involving esoteric equipment or techniques before a new product can be qualified. And finally, there are the administrative issues associated with bringing any new product into inventory, which can include everything from purchasing to EH&S, to supply chain and logistics. While no supplier can wave a magic wand to completely eliminate all the steps in the replacement process, large suppliers who are dedicated to the industry can offer significant assistance that can shorten the timetable. This article summarizes some of the work done at The Dow Chemical Co. to identify and develop suitable replacements for Exxate 600, 700, 800, 900, 1000, 1200 and 1300 in solventborne coatings.

What are Exxate Solvents?

The Exxate line of solvents includes those noted above. Each Exxate solvent is composed of a mixture of branched and linear alkyl acetates. They are commonly referred to as oxo-alkyl acetates. The number in the Exxate solvent name refers to the number of carbons on the alkyl chain of the ester. Exxate 600 is a mixture of six carbon alkyl acetate esters, Exxate 700 a mixture of primarily seven carbon alkyl acetate esters, and so on.

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Figure 2/Evaporation profile of n-butyl acetate compared to n-propyl propionate/n-butyl propionate blend

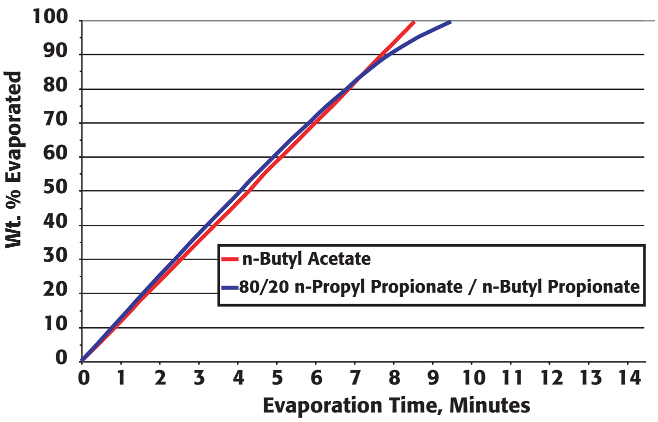
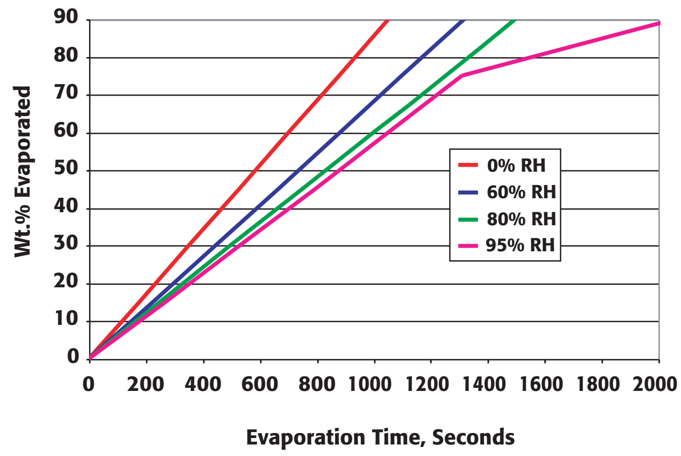


Figure 3/n-butanol: effect of relative humidity on evaporation profile



Use of Exxate Solvents in Solventborne Coatings

Important criteria for solvent selection in solventborne coatings include solvency, ability to reduce coating resin viscosity, evaporation rate, density, odor, regulatory status, cost and other factors, depending on application. Since Exxate solvents are mainly used as the slow or "tail" solvent in coatings, it is most critical to match the evaporation rate as closely as possible. The "tail" solvent slows the drying of the coating, allowing time for it to flow and level, thereby improving the film appearance.

When replacing a solvent in a solventborne coating, matching the relative evaporation rate (RER) is critical in maintaining product performance. For single solvent replacements, an assessment can easily be made by comparing the RER values to the Exxate fluid to be replaced. For those Exxate fluids whose RERs are more difficult to match with currently available commercial solvents, blends can be utilized. However, comparing RER values may not lead to a suitable choice. Evaporation profiles, also described as percent of solvent evaporated over time, may differ dramatically for a blend even if the "average RER" is identical. Evaporation profile and evaporation rates for blends can be predicted by a number of modeling programs. Predictions generated by CHEMCOMP[2], a suite of solvent-prediction programs developed by The Dow Chemical Co., illustrates this point. This program is designed to model the solvent blend evaporation behavior that should be observed when using a Shell evaporometer for the ASTM standard evaporation test. For example, n-butyl acetate has the same RER as a blend of 78% (by weight) isopropyl acetate and 22% n-pentyl propionate. This would lead to an assumption that, based on evaporation rate, this blend would be a good replacement for n-butyl acetate. Examination of the predicted evaporation profile shows that this assumption may not be accurate. Figure 1 shows a comparison of the evaporation profile, modeled at 25 °C with a relative humidity of 50%, of n-butyl acetate versus the blend. In this case, the slower solvent of the blend (isopropyl acetate) evaporates much more quickly than the target. Once the isopropyl acetate has evaporated, n-pentyl propionate then evaporates at a much slower rate than the target.

A blend of 80% n-propyl propionate and 20% n-butyl propionate has the same predicted RER as the blend above, but the evaporation profile match is superior (Figure 2).

The evaporation profiles of solvents with greater water solubility are more affected by humidity. For example, Figure 3 shows the evaporation profile for n-butanol (7.7 % soluble in water at 20 °C) at increasing levels of relative humidity. The sharp decrease in rate at 95% relative humidity indicates that n-butanol has completely evaporated, and the water absorbed then evaporates at a slower rate.

Therefore, water solubility of a solvent should be considered when choosing replacements for coatings that will be cured at various environmental conditions.

Recommended Replacements

Recommendations for each Exxate fluid include at least one single solvent recommendation and, for some, a selection of blends. The single solvent recommendation is the closest match based on RER and Hansen solubility parameters. A selection of blends is listed to offer choices that cover various performance, regulatory and cost requirements. For some formulations, these recommendations may offer a direct substitute. However, depending on requirements, adjustment of the solvent blend may be required to achieve the proper solvent balance. Replacement recommendations are based on single solvents and solvent blends that best match evaporation profiles.

CHEMCOMP allows the evaporation profiles to be predicted with various temperature and relative humidity. Conditions in the figures are 25 °C and 50% relative humidity unless otherwise noted.

Exxate 600

A commercially available replacement exists for Exxate 600 that is nearly identical in structure and properties. Comparison of the chemical structure shows that n-pentyl propionate is an isomer of the four components of Exxate 600[3] (See Figure 4).

Table 1 shows the physical properties to be nearly identical. The small differences can be attributed to the fact that most of the Exxate 600 isomers contain branched alkyl groups while UCAR n-Pentyl Propionate contains only linear alkyls. In addition to flash point, evaporation rate and solubility parameters, the table also shows other useful characteristics such as:

• Water solubility — an important factor for water-sensitive formulations or to predict the impact of relative humidity on drying;

• Density — higher-density solvents will contribute more volatile organic chemicals (VOC) for an equivalent volume;

• Surface tension — an important factor for some applications such as plastic coatings;

• HAP — HAP (Hazardous Air Pollutant) status as defined by the U.S. EPA Resistivity — important for electrostatically applied coatings.

In many cases, n-pentyl propionate can be used as a drop-in replacement for Exxate 600. Comparison of evaporation rates shows very similair profiles, although n-pentyl propionate may evaporate slightly faster (Figure 5).

The higher Exxate fluids, Exxate 700 and above, are unique in their physical properties compared to other commercially available solvents, and thus may be more challenging to replace. Tables 2 through 6 show physical properties of Exxate fluids compared to recommended solvents and solvent blends. Some formulations may require a blend to achieve desired performance. The comparative evaporation profiles are given for each set of replacement recommendations. The proper balance of solvent properties, i.e. evaporation rate, solubility parameters, water solubility, density, surface tension, resistivity, HAP status and cost can be evaluated for individual needs. Evaluation of the properties of each recommendation can assist in selection of the proper solvent for different application requirements.

Figure 4/Comparison of molecular structures of Exxate 600 isomers and n-pentyl propionate

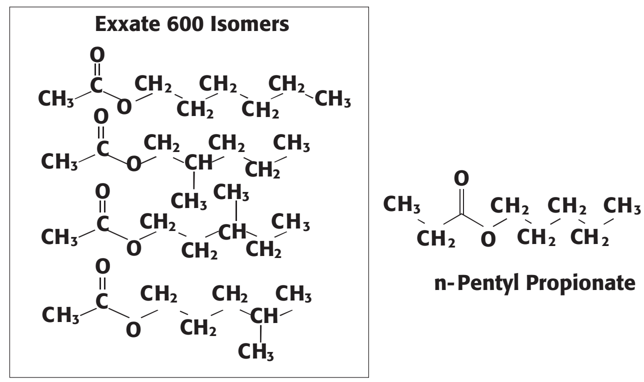
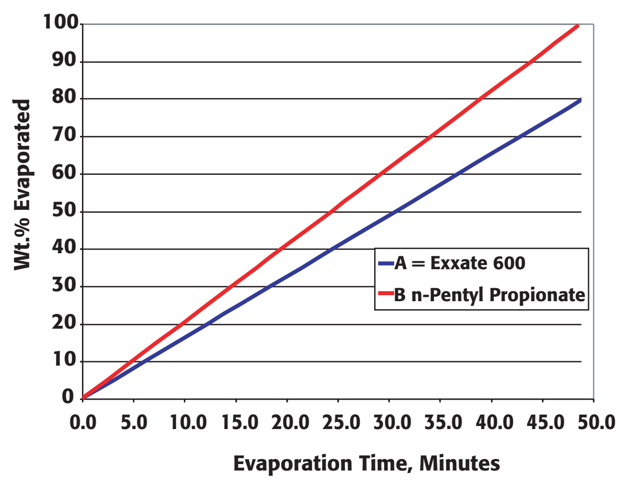


Table 1/Exxate 600 and n-pentyl propionate property comparison

Property		Exxate 600	n-Pentyl Propionate
Solubility in water, weight %		<0.05	<0.05
RER, n-BuAc=1		0.17	0.2
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	14.5	15.6
	polar	7.0	5.1
	h-bonding	5.3	5.1
Density, lb/gal		7.3	7.28
Surf.Tension, dynes/cm		25	26.4
HAP		N	N
Resistivity		High	High

Figure 5/Exxate 600 evaporation profile comparison



Abbreviations and supplier nomenclature:

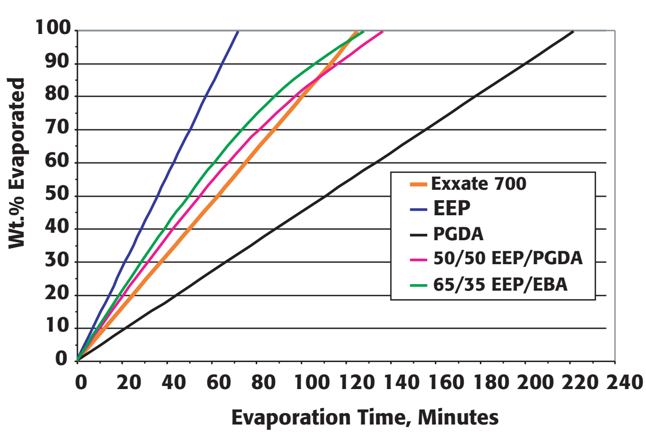
EEP = ethyl 3-ethoxy propionate
UCAR[4] Ester EEP, EASTMAN[5] EEP Solvent
2-EHAc = 2-ethylhexyl acetate
PGDA = propylene glycol diacetate
DOWANOL[6] PGDA,
EBA = ethylene glycol butyl glycol ether acetate
Butyl CELLOSOLVE[7] acetate, EASTMAN EB acetate, glycol ether EB acetate
n-BuAc = n-butyl acetate
DPMA = dipropylene glycol methyl ether acetate
DOWANOL DPMA, ARCOSOLV[8] DPMA
IBHK = isobutyl heptyl ketone
ECOSOFT[9] Solvent IK
DBA = diethylene glycol butyl ether acetate
Butyl CARBITOL[10] acetate, EASTMAN DB acetate, glycol ether DB acetate
TPMB = 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate
UCAR Filmer IBT, TEXANOL[11] Ester Alcohol

Exxate 700

Table 2/Exxate 700 replacements physical property comparison

Property		Exxate 700	EEP	PGDA	50% EEP + 50% PDGA	65% EEP + 35% EBA
Sol. (in H_2O, wt%)		0.01	5.2	7.4	5.2 / 7.4	5.2/1.6
RER, n-BuAc=1		0.08	0.12	0.04	0.07	0.07
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	14.5	16.2	15.8	16	16.3
	polar	6.8	3.3	3.5	3.3	3.7
	h-bonding	4.7	8.8	8.8	8.8	8.8
Density, lb/gal		7.28	7.91	8.77	8.3	7.8
Surf.Tension, dynes/cm		26	28.1	32.5	28.1/32.5	28.1/27.4
HAP		N	N	N	N	35% Y
Resistivity		High	High	High	High	High

Figure 6/Exxate 700 evaporation profile comparison

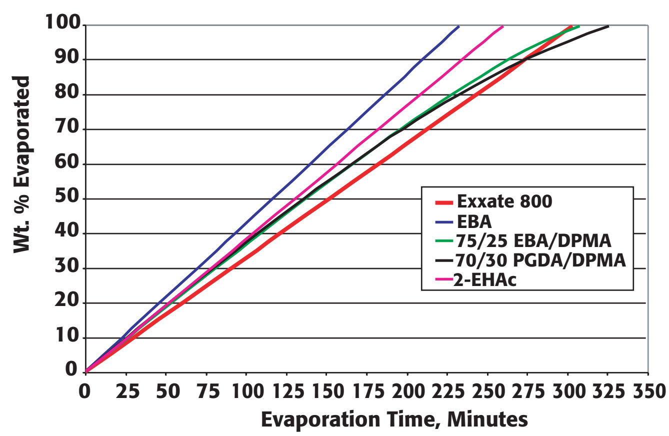


Exxate 800

Table 3/Exxate 800 replacements physical property comparison

Property		Exxate 800	EBA	2-EHA	75% EBA + 25% DPMA	30% DPMA + 70% PGDA
Sol. (in H_2O, wt%)		<0.1	1.6	0.03	1.6 / 16	16 / 7.4
RER, n-BuAc=1		0.03	0.04	0.03	0.03	0.03
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	14.7	16	15.8	16.1	15.9
	polar	6.5	4.5	2.9	4.6	3.9
	h-bonding	4.1	8.8	5.1	8.6	8.5
Density, lb/gal		7.3	7.8	7.27	7.9	8.5
Surf.Tension, dynes/cm		26	27.4	25.8	27.7/27.3	27.3/32.5
HAP		N	Y	N	75% Y	N
Resistivity		High	High	High	High	High

Figure 7/Exxate 800 evaporation profile comparison

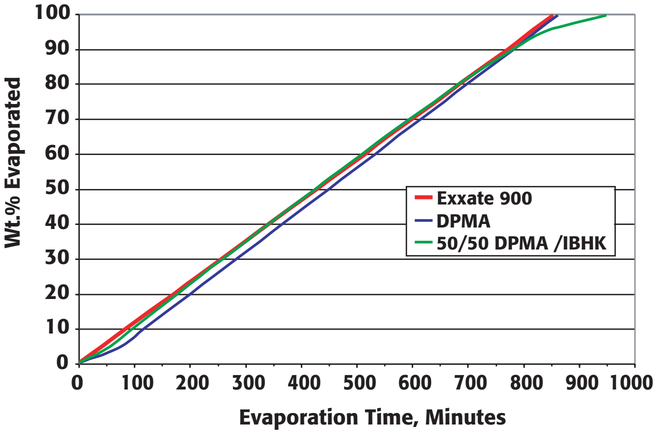


Exxate 900

Table 4/Exxate 900 replacements physical property comparison

Property		Exxate 900	DPMA	50% IBHK + 50% DPMA
Sol. (in H_2O, wt%)		0.02	16	0/16
RER, n-BuAc=1		0.01	0.015	0.01
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	14.7	16.3	15.7
	polar	5.9	4.9	4.9
	h-bonding	3.7	8	6.4
Density, lb/gal		7.3	8.13	6.7
Surf.Tension, dynes/cm		27	27.3	26.8 / 23.2
HAP		N	N	N
Resistivity		High	High	Medium

Figure 8/Exxate 900 evaporation profile comparison

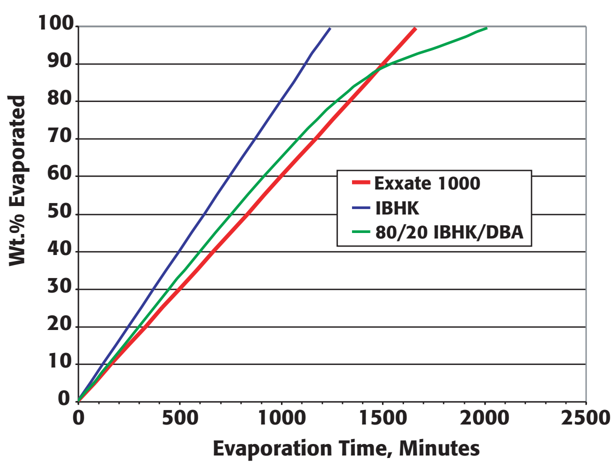


Exxate 1000

Table 5/Exxate 1000 replacements physical property comparison

Property		Exxate 1000	IBHK	20% DBA + 80% IBHK
Sol. (in H_2O, wt%)		0	0.002	4/0
VP (mmHg@20°C)		0.1	0.03	
RER, n-BuAc=1		0.006	0.007	0.004
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	14.9	15.2	15.3
	polar	5.7	4.9	4.8
	h-bonding	3.1	5	5.6
Density, lb/gal		7.3	6.8	7.1
Surf.Tension, dynes/cm		27.5	26.8	30 / 26.8
HAP		N	N	20% Y
Resistivity		High	Medium	Medium

Figure 9/Exxate 1000 evaporation profile comparison

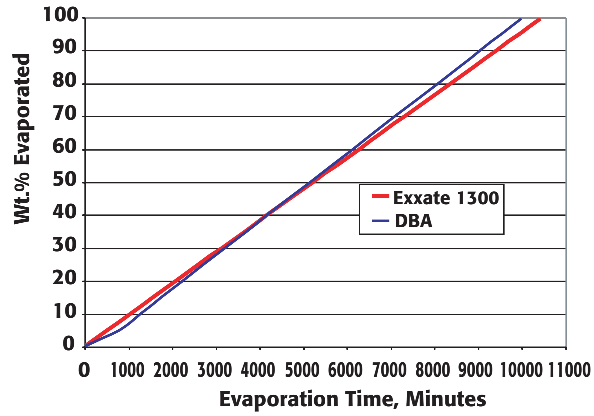


Exxate 1200 and 1300

Table 6/Exxate 1200 and Exxate 1300 replacements physical property comparison

Property		Exxate 1200	TPMB	Exxate 1300	DBA
Sol. (in H_2O, wt%)		NA	0	NA	4
VP (mmHg@20°C)		NA	0.01	0.03	<0.01
RER, n-BuAc=1		.003*	0.002	0.001	0.0012
Hansen Sol. Par. $(J/cm^3)^{1/2}$	dispersion	15.1	15.1	15.1	16.0
	polar	5.1	6.1	5.1	4.1
	h-bonding	1.6	9.8	1.6	8.2
Density, lb/gal		7.3	7.89	7.3	8.14
Surf.Tension, dynes/cm		NA	30.7	28	30
HAP		N	N	N	Y
Resistivity		High	Medium	High	High

Figure 10/Exxate 1300 evaporation profile comparison (0% RH)



Note: Evaporation rate profile comparison for Exxate 1200 is currently unavailable in the CHEMCOMP database due to the unavailability of physical property data.

Summary

There are several options available to the coatings formulator for replacing Exxate solvents. Whether the solution is a direct replacement or requires adjusting the solvent balance, formulators have many options in order to maintain product performance and cost effectiveness. ⊕

References

1 Exxate is a trademark of ExxonMobil Chemical Co.
2 CHEMCOMP is a Service Mark of The Dow Chemical Co.
3 Carter, W.P.L. (2000). Atmospheric Ozone Impacts of Exxsol D95, Isopar M and the Exxate fluids. Final Report. ExxonMobil. RT3L.
4 UCAR is a trademark of The Dow Chemical Co.
5 EASTMAN is a trademark of The Eastman Chemical Co.
6 DOWANOL is a trademark of The Dow Chemical Co.
7 CELLOSOLVE is a trademark of The Dow Chemical Co.
8 ARCOSOLV is a trademark of Lyondell Chemical Co.
9 ECOSOFT is a trademark of The Dow Chemical Co.
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11 TEXANOL is a trademark of Eastman Chemical Co.