UCAR™ n-Alkyl Propionates

Oxygenated Solvents

UCAR™ n-Alkyl Propionates

Non-HAPs Solvent for Coatings & Printing Inks

Introduction

UCAR™ n-Alkyl Propionates provide a combination of properties that are desired in active solvents for high-solids coatings and printing inks. These solvents show viscosity reductions in coating formulations that are more effective than commercial n-alkyl acetate esters. The solvency power of solvents with branched structures is not as strong as it is in linear chain solvents. The linear structures of UCAR™ n-Alkyl Propionates contribute to effective viscosity reduction, while also improving solvent diffusion from coating films. Odor characteristics are also significantly more favorable than with other solvents of similar volatility. The high electrical resistivity properties provide advantages in formulating high-solids coatings for electrostatic spray applications.

The UCAR™ n-Alkyl Propionates family includes UCAR™ n-Propyl Propionates, UCAR™ n-Butyl Propionate and UCAR™ n-Pentyl Propionates. These three products encompass a range of evaporation rates – from fast to slow – making them suitable for a variety of applications. Typical applications for coatings formulated with alkyl propionates are automotive refinish, OEM, and appliance coatings. These alkyl propionate solvents are listed on the TSCA inventory. They are not listed as Hazardous Air Pollutants (HAPs) under Title III of the Clean Air Act.

Special Features

- Non-HAPs
- Stronger solvency than acetate esters in high-solids coatings
- Proper volatility for high-solids coatings and printing ink applications
- Linear structure, enabling faster diffusion than branched-chain esters through coating and ink films
- High electrical resistivity for electrostatically-sprayed coatings
- Low odor values
- Polymerization solvents

The strong solvency, high electrical resistivity, low surface tension, and the relative evaporation rates of UCAR™ n-Propyl, n-Butyl and n-Pentyl Propionate make them ideal candidates for use in high-solids compliant coatings. Their strong solvency results in excellent viscosity reduction, high solids, and lower VOC formulations. High electrical resistivity provides excellent transfer efficiency and wrap-around for electrostatic spray-applied coatings. Low surface tension gives improved substrate and pigment wetting action.

The high boiling point and good chain transfer activity of UCAR™ n-Pentyl Propionate make it an excellent polymerization medium for high-solids acrylic resins. Resin solutions prepared in UCAR™ n-Pentyl Propionate have low molecular weights, narrow molecular weight distributions, lower viscosities, and excellent clarity.

UCAR™ n-Propyl, n-Butyl and n-Pentyl Propionates have lower odor values than acetate esters, such as n-butyl acetate are oxo-hexyl acetate, and many ketones.

Special Features cont'd

UCAR™ n-Alkyl Propionates are ideal alternatives for three solvents commonly used in coatings and printng inks:

- UCAR™ n-Propyl Propionate is an excellent replacement for xylene.
- UCAR™ n-Butyl Propionate is an excellent replacement for methyl n-amyl ketone (MAK).
- UCAR™ n-Pentyl Propionate is an excellent replacement for oxo-hexyl acetate.

Chemical Structures

$CH_3CH_2CH_2O\text{-}C(=O)\text{-}CH_2CH_3$
UCAR™ n-Propyl Propionate

$CH_3CH_2CH_2CH_2O\text{-}C(=O)\text{-}CH_2CH_3$
UCAR™ n-Butyl Propionate

$CH_3CH_2CH_2CH_2CH_2O\text{-}C(=O)\text{-}CH_2CH_3$
UCAR™ n-Pentyl Propionate

Comparative Physical Properties

Property	UCAR Propyl Propionate	UCAR Butyl Propionate	UCAR Pentyl Propionate
Molecular Weight	116.2	130.2	144.2
Specific Gravity at 20/20°C	0.881	0.876	0.874
Density at 20°C, g/L (lb./gal.)	7.34	7.30	7.28
Relative Evaporation Rate (RER), Where n-butyl acetate=1	1.2	0.45	0.2
Solubility Parameters (Hansen Method)			
Total	8.6	8.4	8.3
Nonpolar	7.6	7.5	7.6
Polar	1.8	1.6	1.4
Hydrogen Bonding	3.6	3.3	3.2
Boiling Point, °C	122.4	144.7	164.9
Closed Cup Flash Point, °F	75	100	135
Freezing Point, °C	-76	<-75	<-75
Vapor Pressure at 20°C, mmHg	10.7	3.4	1.5
Viscosity at 20°C, cP	0.68	0.83	1.04
Solubility in Water at 20°C, by wt%	0.5	0.2	<0.5
Surface Tension at 20°C, dynes/cm	24.7	25.3	26.4
Electrical Resistivity, megaohm	>1,000	>1,000	>1,000

Performance

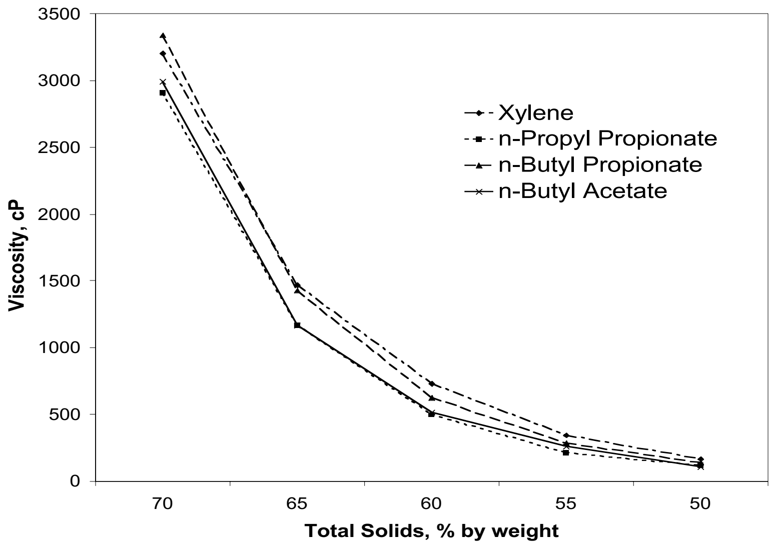
High-Solids Coatings

Federal and state emission regulations have placed increasingly strict limits on the level of Volatile Organic Compounds (VOC) permissible in industrial product finishes. The coatings industry has classically dealt with this demand in a variety of ways. One method is by converting to waterborne coatings; another uses lower solvent level or high-solids coatings to achieve compliance. These high-solids coatings require solvents that provide traditional coating properties at reduced volume levels. Therefore, for a coating to function properly, the solvent must have high solvency power. A measure of the solvency power of a solvent is its efficacy in reducing the viscosity of a polymer. The viscosity reduction capabilities of the UCAR™ n-Alkyl Propionates – in comparison with xylene, methyl n-amyl ketone and oxo-hexyl acetate – were evaluated in a commonly used high solids acrylic resin.(1) Results are shown in Figures 1 and 2.

(1) Acryloid™ AT-400, in methyl n-amyl ketone.

Figure 1 – Viscosity Profiles of Solvents in High Solids Acrylic Resin

UCAR™ n-Alkyl Propionates and Xylene



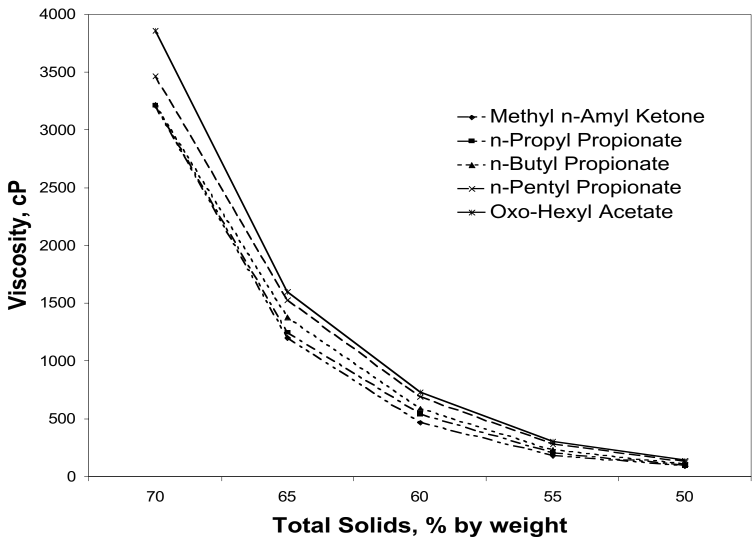
The data used to generate Figure 1 are shown in Table 1.

Table 1 – Brookfield Viscosity Data

		Viscosity, cP				
Solvent	**Total Solids**	**70%**	**65%**	**60%**	**55%**	**50%**
Xylene		3202	1470	733	344	167
n-Propyl Propionate		2907	1170	499	212	120
n-Butyl Propionate		3340	1430	630	289	143
n-Butyl Acetate		2997	1170	519	262	111

Figure 2 – Viscosity Profiles of Solvents in High Solids Acrylic Resin

UCAR™ n-Alkyl Propionates, Methyl n-Amyl Ketone and Oxo-Hexyl Acetate



The data used to generate Figure 2 are shown in Table 2.

Table 2 – Brookfield Viscosity Data

		Viscosity, cP				
Solvent	**Total Solids**	**70%**	**65%**	**60%**	**55%**	**50%**
Methyl n-Amyl Ketone		3210	1200	468	184	93
n-Propyl Propionate		3215	1250	545	205	100
n-Butyl Propionate		3220	1380	591	234	110
n-Pentyl Propionate		3470	1530	693	284	134
Oxo-Hexyl Acetate		3860	1600	735	306	144

The data was obtained by adding each solvent separately, in increments of 5% by weight, to the polymer and then measuring the viscosity. The lower the viscosity at any particular total solids level, the more efficient (and desirable) the solvent. At equal viscosities, the data shows which solvent provides the highest total solids, or least amount of solvent needed, thereby providing lower VOC levels and ultimately, fewer emissions to the atmosphere. The effectiveness of the UCAR™ n-Alkyl Propionates in viscosity reduction is apparent in both Figures 1 and 2, which depict viscosity vs. total solids of the high solids acrylic resin. Figure 1 shows UCAR™ n-Propyl Propionate, UCAR™ n-Butyl Propionate and n-butyl acetate in comparison with xylene. The results indicate that UCAR™ n-Propyl Propionate is an excellent replacement for xylene. Figure 2 depicts the UCAR™ n-Alkyl Propionates in comparison with methyl n-amyl ketone (MAK) and oxo-hexyl acetate. Methyl n-amyl ketone (MAK), a commonly used solvent in high-solids coatings, is effective in reducing the viscosity of the system because of its high solvency power. Next in viscosity reduction power is UCAR™ n-Propyl Propionate, followed by UCAR™ n-Butyl Propionate and then by UCAR™ n-Pentyl Propionate. The least effective is oxo-hexyl acetate. The superior viscosity reduction ability of the UCAR™ n-Alkyl Propionates compared to oxo-hexyl acetate is due to their lower neat viscosities, and to their linear (non-branched) molecular structures. The commercial grade of oxo-hexyl acetate is a mixture containing branched isomers. Studies have shown that solvents having branched structures result in higher coatings viscosities than those with linear structures like the UCAR™ n-Alkyl Propionates.

The limits on a coating's VOC level are expressed in weight of volatiles per volume of liquid coating. This makes the use of lower density solvents more attractive since they provide more volume per unit weight. These two criteria of solvency power and relatively low densities make UCAR™ n-Alkyl Propionates ideal candidates for use in high-solids coatings. The densities of commonly used solvents are show in Table 3.

Table 3 – Densities of High-Solids Coatings Solvents

Solvents	Density, lb/gal	VOC
Ketones		
Methyl Isobutyl Ketone (MIBK)	6.67	Lowest
Diisobutyl Ketone (DIBK)	6.72	
Methyl n-Amyl Ketone (MAK)	6.81	
Alcohol		
n-Butanol	6.76	
Alkyl Esters		
UCAR™ n-Propyl Propionate	7.34	
UCAR™ n-Butyl Propionate	7.30	
UCAR™ n-Pentyl Propionate	7.28	
Primary Amyl Acetate	7.29	
UCAR™ n-Butyl Acetate	7.34	
Ether Esters		
UCAR™ Ester EEP	7.91	Highest

Electrical Resistivity

In addition to high solvency and low density, another important consideration in the selection of solvents for use in high-solids coatings is the electrical resisitivity of the solvents. UCAR™ n-Propyl, n-Butyl and n-Pentyl Propionates have electrical resisitivity values of greater than 100 megaohms. This property allows the coating formulator to achieve the electrical resisitivity necessary to obtain high tranfser efficiency and wrap-around by electrostatic spray. Many of the ingredients used in coatings, such as alcohols or catalysts used to promote crosslinking, decrease the electrical resisitivity of those coatings. This can make it difficult to obtain all the desired properties and still have the electrical resistivity necessary to achieve good transfer efficiency by electrostatic spray. Compared to solvents such as ketones, the higher values for UCAR™ Alkyl Propionates allow greater formulation flexibility in selecting other ingredients while maintaining the required electrical resistivity of the coatings. A list of solvents by class and electrical resisitivity properties is shown in Table 4.

Table 4 – Electrostatic Spray Solvent Resistivities

Solvent	Electrical Resistivity, megaohms	
Hydrocarbons	>1,000	High
UCAR™ n-Alkyl Propionates	>1,000	
Acetate Esters	0.03 to >20	
Ketones	0.03 to 1.50	
Glycol Ethers	0.02 to 0.45	
Alcohols	0.03 to 8.0	Low

Surface Tension

High-solids coatings tend to have higher surface tensions than do low-solids coatings. High surface tensions can cause poor spray patterns and atomization, poor wetting of the coating on a substrate, and such film deficiencies as fish eyes and edge pull. Surface tension can be reduced by the addition of silicone surfactants or organic-based surfactants; however, these additives sometimes interfere with the adhesion and water resistance properties of a coating. The low surface tension of UCAR™ n-Alkyl Propionates can help control the surface tension of the coating and therefore allow for more flexibility in formulations. Surface tension values for various solvents are given in Table 5.

Table 5 – Surface Tension of Solvents Used in High-Solids Coatings

Solvent	Surface Tension, dynes/cm At 20° C
Ketones	
Diisobutyl Ketone (DIBK)	23.2
Methyl Isobutyl Ketone (MIBK)	24.0
Methyl n-Amyl Ketone (MAK)	26.7
Diacetone Alcohol	30.3
Esters	
Isobutyl Acetate	23.4
Ethyl Acetate	23.8
UCAR™ n-Propyl Propionate	24.7
UCAR™ n-Butyl Propionate	25.3
n-Butyl Acetate	25.3
Primary Amyl Acetate	25.8
UCAR™ n-Pentyl Propionate	26.4
UCAR™ Ester EEP	28.1

Polymerization Solvent

With the advent of high-solids coating technology, lower molecular-weight resins are being developed to keep the viscosity increase to a minimum as the solids content of a coating increases. Two important features of a solvent to be used as a polymerization medium for acrylic resins are boiling point and chain transfer ability. In general, the higher the polymerization temperature, the lower the average molecular weight of the polymer. Similarly, the higher the chain transfer ability (i.e., the tendency of the solvent to abstract a radical from the growing chain of the polymer, thus terminating the chain and initiating a new polymer chain), the lower the average molecular weight of the polymer.

The high boiling point of UCAR™ n-Pentyl Propionate is an advantage in acrylic polymerization, enabling the production of low molecular weight and low viscosity resins. Resins prepared in this solvent exhibit excellent molecular weight and viscosity characteristics, as well as clarity and color. The following example demonstrates the use of UCAR™ n-Pentyl Propionate in the polymerization of an acrylic resin.

The acrylic copolymer composition is shown in Table 6. Table 7 illustrates the molecular weights and polydispersivity (molecular weight distribution) for resins prepared in UCAR™ n-Pentyl Propionate and oxo-hexyl acetate. Slightly better viscosity is obtained with UCAR™ n-Pentyl Propionate than with oxo-hexyl acetate (a hazy resin).

Table 6 – Acrylic Copolymer Composition

Ingredients	Weight Percent
Monomer	
Butyl Acrylate	33
2-Hydroxethyl Methacrylate	14
Methyl Methacrylate	14
Styrene	7
Acrylic Acid	2
Solvent	30
Total	100

Table 7 – Acrylic Copolymer Properties

Property	UCAR™ n-Pentyl Propionate	Oxo-Hexyl Acetate
Viscosity at 70% Total Solids, cP	1320	1530
Mw	6600	6720
Mn	2880	2970
Mw/Mn	2.29	2.27
Polymerization Temperature, °C	162	162

The ultimate effect of these desirable resin properties (low molecular weight, narrow molecular weight distribution, and low viscosity) is a high-solids coating with good film properties (see Table 8). Compared to oxo-hexyl acetate, UCAR™ n-Pentyl Propionate exhibits better gloss and sharper distinctness of image. Other coating physical properties are comparable.

Table 8 – Acrylic Copolymer Coatings Film Properties(2)

Property	UCAR™ n-Pentyl Propionate	Oxo-Hexyl Acetate
Gloss, 20°	85	79
Distinctness of Image, %	70	60
Crosshatch Adhesion, %	100	100
MEK Rubs	100+	100+
Pencil Hardness	3H	4H

(2) Cured at 300°F for 20 minutes. Dry film thickness of 1.0 to 1.1 mil on steel panels.

UCAR™ n-Butyl Propionate can also be used in polymerization processes, especially as an alternative for MAK. Polymers prepared in MAK can develop color during the polymerization process due to the ketone moiety in MAK. Polymers prepared in UCAR™ n-Butyl Propionate do not develop color due to the inherent stability of the ester group. This attribute of UCAR™ n-Butyl Propionate makes it an excellent solvent for conducting polymerization reactions.

Solvent Odor Characteristics

Odor threshold values for UCAR™ n-Propyl, n-Butyl and n-Pentyl Propionate, n-butyl acetate, xylene, methyl n-amyl ketone, and oxo-hexyl acetate were determined.

Odor potential is expressed as odor detection threshold values. Odor potentials were calculated by determining the ED_{50} of each solvent. The solvents were evaluated using the standard test procedures for evaluating the odor potential for neat solvents. Two methods were used for each evaluation. The first utilized the dry gas meter as the vaporization mechanism; the second used a conventional spray gun as the vaporization mechanism. Solvents were vaporized and captured in a “Tedlar” sampling bag.

ED_{50} is a dilution ratio equal to odor units at a level where 50 percent of the panelists can detect the odor. ED_{50} is used as a guide to determine the dilutions needed for a particular sample. It the sample has an ED_{50} of 200, this means the sample needs 200 parts of non-odorous air to dilute 1 part of odorous air to the point where 50 percent of the population detects the odor and 50 percent does not detect the odor.

The spray and dry gas odor potential ED_{50} values are shown in Table 9. The solvents are ranked in order of increasing odor detection threshold values by the spray method, which more closely simulates the use of solvents in coating applications. Hydrocarbon solvents typically have a low odor detection thresholds. However, in tests using the conventional spray method, UCAR™ n-Propyl Propionate had the lowest odor detection value of all the evaluated solvents. In fact, both n-Propyl and n-Butyl Propionate have lower values than xylene. Overall, the UCAR™ n-Alkyl Propionates have lower values than solvents having similar relative evaporation rates.

Table 9 – Summary of ED_{50} Calculations(3)

	ED_{50}	
Solvent	**Spray**	**Dry Gas**
UCAR™ n-Propyl Propionate	106	136
UCAR™ n-Butyl Propionate	250	236
Xylene	302	124
UCAR™ n-Pentyl Propionate	453	375
Methyl n-Amyl Ketone	459	474
n-Butyl Acetate	531	342
Oxo-Hexyl Acetate	919	520

(3) Data by Emissions Evaluation Center, Eastern Michigan University

Product Safety

When considering the use of any Dow products in a particular application, you should review our latest Material Safety Data Sheets and ensure that the use you intend can be accomplished safely. For Material Safety Data Sheets and other product safety information, contact the Customer Information Group. Before handling any other products mentioned in the text, you should obtain available product safety information and take necessary steps to ensure safety of use.

Classification/ Registry Numbers

UCAR™ n-Butyl Propionate
CAS 590-01-2
EINECS 2096695

UCAR™ n-Pentyl Propionate
CAS 624-54-4
EINECS 2108527

UCAR™ n-Propyl Propionate
CAS 106-36-5
EINECS 203-389-7

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