Replacing Dirty and Toxic with Clean and Green

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Introduction

Most traditional, organic solvents that are utilized daily in industrial, commercial and academic settings are known to be toxic to the end-user and detrimental to the environment. National and local regulatory authorities are continually tightening regulations to curtail the use of these toxic chemicals.

This paper introduces six new solvents developed by TBF Environmental Technology Inc. These new solvents have been carefully formulated to mimic as closely as possible the performance of traditional chemicals, without their toxic and polluting properties. They may effectively replace some of the frequently used traditional organic solvents that are increasingly being phased out of use by new regulations.

Factors to Consider

When evaluating the safety and quality of a new product, many different factors with respect to the safety, environmental impact, and performance must be considered. There are several methods to classify the toxicity and environmental hazard of a chemical. The terms and classifications that are commonly employed by regulatory authorities and recur in this discussion are defined below.

Volatile Organic Compound (VOC)**:** VOCs are organic chemicals with a high vapour pressure, resulting in a low boiling point, which can engage in photochemical reactions in the atmosphere to form ground-level ozone, a precursor to smog. A small number VOCs are classified as "VOC-exempt" by regulatory authorities in North America, because they pose a low hazard risk for ground-level ozone formation. VOC-exempt solvents are not regulated. VOCs that are not exempt are regulated and are typically present in combination with other components in a formulation. The VOC content of the formulations are reported in quantities of grams of VOC per liter of solution (g/L), of which the solvent is often the largest contributor.

Maximum Incremental Reactivity (MIR): MIR is a quantifiable measure of relative ground-level ozone impacts of VOCs, and is thus used in a quantitative sense to define the environmental hazard when comparing one VOC to another. The MIR values of VOCs were developed by Dr. William Carter at University of California, Riverside as a method of ranking VOCs by their reactive potential. The MIR scale was initially adopted by the California Air Resources Board (CARB) and is now being considered by the Environmental Protection Agency (EPA). Measured in grams ozone per gram VOC (g O_3 / g VOC), a lower MIR value indicates a lower potential for reactivity with respect to the formation of ground-level ozone and harmful compounds.

Acute Toxicity (LD_{50}): LD_{50} is defined as the lethal dose, given all at once, required to kill 50% of a test population. When comparing toxicities of different compounds, a lower LD_{50} indicates less chemical required to produce lethality, and is thus the more toxic the compound. Acute toxicities are generally measured by oral, dermal or inhalation mechanisms as tested on specific animals such as rats, fish and crustaceans. This discussion focuses on the acute oral LD_{50} of various chemicals, measured in mg/kg for the test animal reported.

Permissible Exposure Limits (PEL) and Threshold Limit Values (TLV): PELs and TLVs are restrictions set by regulatory bodies for a specific chemical, measured in parts-per-million (ppm) that quantify the maximum allowable exposure over an 8-hour time weighted average. Many PELs and TLVs are regulated by the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial

Hygienists (ACGIH), or alternatively can be set by the employer as an Occupational Exposure Limit (OEL). A higher value for PEL or TLV indicate lower safety hazards for workers using the product.

PEL and TLV may assist in characterizing the safety and environmental impact of a product. However, in order to be successful, it is imperative that any new product have similar or superior physical properties to the chemical that is being replaced. Physical properties that were carefully considered in the development of TBF Environmental included optimizing the performance of the following key parameters:

- Boiling point - initial temperature, or temperature range, where a phase change occurs that results in the vapourization of a liquid.
- Flash point - the minimum temperature where a volatile compound can form ignitable vapours. Solvency (Kauri Butanol value) - a standardized measure of a solvent's ability to dissolve certain materials. A higher Kauri Butanol (Kb) value indicates greater solvency.
- Hansen Solubility Parameters (HSP) - parameters that quantify the diffusion, polarity, and hydrogen bonding capabilities of a solvent. The HSPs may assist in determining the ability of a solvent to dissolve a certain substance, or to compare the solubilizing abilities of two different solvents.

TBF Environmental Technology Inc.'s new VOC-compliant solvents are compared below to those solvents that they were formulated to replace.

ShiraSol™

ShiraSol was formulated as a replacement for Mineral Spirits and other slow evaporating organic solvents that are used in paint formulations and as paint thinners. ShiraSol can also be used as a replacement solvent or co-solvent for Aromatic 100, Methyl Amyl Ketone (MAK), Perchloroethylene (Perc) and n-Butyl Acetate (nBAc). The following table summarizes the enhanced environmental and safety attributes of TBF Environmental's ShiraSol product as compared to these solvents.

	ShiraSol	**Mineral Spirits**	**Aromatic 100**	**MAK**	**Perc**	**nBAc**
Environmental						
VOC Content: US EPA (outside SCAQMD)	**0**	100%	100%	100%	100%	100%
VOC Content: SCAQMD	**2.9* g/L**	100%	100%	100%	100%	100%
MIR (g O_3 / g organics)	**0.097**	0.9-2.47	7.51	2.80	0.04	0.89
Safety						
Acute Toxicity (Oral LD_{50}, rat, mg/kg)	**13,000**	> 5000	3492	1600	2630	14,130
Exposure Limit	**None Listed**	100 ppm (Cal/OSHA PEL)	19 ppm (OEL)	50 ppm (ACGIH TLV)	25 ppm (ACGIH TLV)	150 ppm (ACGIH TLV)
Flash point (°C)	**43.5**	42	41 - 46	39	-	27
	(110.3 °F)	(108 °F)	(106 - 115 °F)	(102 °F)		(81 °F)

*ASTM Test Method 313-91. South Coast Air Quality Management District (SCAQMD) considers <5 g/L VOC content to be "zero VOC".

ShiraSol is 100% comprised of solvents considered to be VOC-exempt by the EPA, CEPA, NPRI and SCAQMD and as such is considered zero VOC.

ShiraSol is currently the only solvent alternative for Mineral Spirits that is comprised of 100% VOC-exempt material. It also has a far lower MIR value than Mineral Spirits, Aromatic 100, MAK and nBAc.

The component with the highest toxicity in ShiraSol has an acute oral LD50 (rat) value of 13,000 mg/kg, which is significantly higher than the equivalent toxicities for Mineral Spirits, Aromatic 100, MAK and Perc. Perchloroethylene is also a suspected carcinogen. Furthermore, none of the components present in the ShiraSol formulation are regulated by exposure limits dictated by OSHA or ACGIH. By contrast, the California Division of OSHA (Cal/OSHA) limits the exposure of Mineral Spirits (listed as Stoddard Solvent) to 100 ppm. The ACGIH lists TLVs for MAK, Perc and nBAc at 50, 25, and 150 ppm, respectively. ExxonMobil, a manufacturer of Aromatic 100, lists an OEL of 19 ppm. Finally, the flash point for ShiraSol is 43.5 °C, which is close to that of Mineral Spirits, Aromatic 100 and MAK, and is higher than the flash point of nBAc.

	ShiraSol	**Mineral Spirits**
Physical Properties		
Initial Boiling Point (°C)	**147.5**	140 - 158
Evaporation Rate (nBAc = 1)	**0.1**	0.1 - 0.13
Kauri Butanol (Kb) **Value**	**54.5**	33
Surface Tension (dynes/cm)	**24.5**	24.7

As ShiraSol was carefully designed to mimic the physical properties and performance characteristics of Mineral Spirits, the boiling point, evaporation rate and surface tension for ShiraSol are very close to that of many types of Mineral Spirits, which easily allows a user to replace Mineral Spirits with ShiraSol. Additionally, the Kauri Butanol value of ShiraSol is greater than that of Mineral Spirits, and is thus a more effective solvent with respect to solvency.

ShiraSol is currently the only replacement for Mineral Spirits that is zero-VOC, low in toxicity, has a good safety profile, and mimics the physical properties of Mineral Spirits.

EkaSol 1™ and TergoSol™

EkaSol 1 and TergoSol were specifically formulated as replacements for Methyl Ethyl Ketone (MEK) and Acetone. The following table compares the environmental, safety and performance characteristics for the four solvents.

	EkaSol 1	**TergoSol**	**MEK**	**Acetone**
Environmental				
VOC Content: US EPA (outside SCAQMD)	**0**	**0**	100%	exempt
VOC Content: SCAQMD	**2.66***	**2.82***	100%	exempt
MIR (g O_3 / g organics)	**0.47**	**0.065**	1.48	0.43
Safety				
Acute Toxicity (Oral LD_{50}, rat, mg/kg)	**> 5000**	**> 5000**	2737	5800
Flash point (°C)	**5 (41 °F)**	**4.5 (40 °F)**	-9 (16 °F)	-20 (-4 °F)
Physical Properties				

Evaporation Rate (n-Butyl Acetate = 1)	**3.62**	**5.35**	3.86	6.4
Hansen Solubility Parameters $(MPa)^{1/2}$	**19.1**	**18.7**	19.1	19.9
Dispersion (δ_D)	**15.7**	**15.5**	16.0	15.5
Polarity (δ_P)	**6.4**	**6.3**	9.0	10.4
Hydrogen Bonding (δ_H)	**8.5**	**8.1**	5.1	7.0

*ASTM Test Method 313-91. SCAQMD = South Coast Air Quality Management District. EkaSol 1 and TergoSol are a blend of VOC-exempt solvents by EPA and is thus considered Zero VOC by the EPA. EkaSol 1 and TergoSol are considered ultra-low VOC in SCAQMD.

EkaSol 1 and TergoSol are considered zero-VOC by the EPA, and considered ultra-low VOCs in the South Coast Air Quality Management District (SCAQMD), compared to MEK which is a 100% VOC emitter in the United States and Canada including SCAQMD. The MIR of EkaSol 1 is also less than that of MEK, and the MIR of TergoSol is less than the MIR of both MEK and Acetone.

The flash points of EkaSol 1 and TergoSol are greater than those of MEK and Acetone which demonstrates that they are far less flammable. Additionally, the major component of both EkaSol 1 and TergoSol has an acute toxicity (oral LD_{50}, rat) of over 5000 mg/kg, which is higher and therefore less toxic than that of MEK. Studies of chronic exposure have found MEK to be carcinogenic and chronic use can lead to serious developmental and reproductive issues. Although Acetone has a comparable LD_{50} to EkaSol 1 and TergoSol, Acetone has been shown to enhance the toxicity of other chemicals through synergistic toxic effects.

With respect to performance characteristics, the evaporation rate of EkaSol 1 is comparable to the rate of MEK, and the evaporation rate of TergoSol is close to that of Acetone. Additionally, the Hansen Solubility Parameters of EkaSol 1 and TergoSol are similar to that of MEK and Acetone. This gives EkaSol 1 and TergoSol comparable solubilizing capabilities to MEK and are suitable replacements with broad utility in paint, coating, adhesive and ink industries.

ZemaSol™

ZemaSol was formulated as a replacement solvent for Xylenes and Toluene for use in numerous applications. The table below compares the environmental and safety considerations of ZemaSol to Xylenes and Toluene.

	ZemaSol	Xylenes	Toluene
Environmental			
VOC Content: US EPA (outside SCAQMD)	**0**	100%	100%
VOC Content: SCAQMD	**1.59 g/L***	100%	100%
MIR (g O_3 / g organics)	**0.079**	4.25 - 10.71	3.97
Safety			
Acute Toxicity (Oral LD_{50}, rat, mg/kg)	**> 5000**	> 3520	> 5580
Exposure Limits	**> 200 ppm (OSHA PEL)**	100 ppm (OSHA PEL)	10 ppm (Cal/OSHA PEL)

*ASTM Test Method 313-91. South Coast Air Quality Management District (SCAQMD) considers <5 g/L VOC content to be "zero VOC". ZemaSol is 100% comprised of solvents considered to be VOC-exempt by the EPA, CEPA, NPRI and SCAQMD and as such is considered zero VOC.

ZemaSol is comprised solely of VOC-exempt solvents as determined by the EPA and SCAQMD, and is therefore considered to be a zero-VOC product. Xylenes and Toluene are both 100% VOC emitters. Furthermore, the MIR value for ZemaSol is over 50 times lower than the values for Xylenes and Toluene, and therefore contains less reactive potential for the formation of ground-level ozone that is detrimental to human health and the environment.

While the acute oral toxicities (LD_{50}, rat) for Xylenes and Toluene are similar to that of ZemaSol, both Xylenes and Toluene are associated with toxic effects derived from chronic exposure. For example, Toluene is designated as a teratogen and reproductive hazard, and Xylenes has been shown to affect the development of fetuses. The main component of ZemaSol has not been shown to have toxic effects other than those derived from acute toxicity.

The following table compares various physical properties between ZemaSol, Xylenes and Toluene. Currently, the most commonly used replacements for Xylenes and Toluene are *para*-Chlorobenzotrifluoride (PCBTF) and *tertiary*-Butyl Acetate (TBAc). These solvents are included in the table.

	ZemaSol	**Xylenes**	**Toluene**	**PCBTF**	**TBAc***
Physical Properties					
Surface Tension (dynes/cm)	**24.2**	28.7	28.4	25	22.4
Density (g/mL)	**1.0**	0.87	0.87	1.34	0.86
Viscosity (cP)	**0.44**	0.81	0.55	0.79	1.2
Kauri Butanol (Kb) **Value**	**90.3**	98	105	64	-

ZemaSol was carefully designed to mimic Xylenes and Toluene in solvency, surface tension and other physical parameters. When compared to the performance characteristics of PCBTF and TBAc, PCBTF is too heavy and has poor solvency, while TBAc is too viscous and has low surface tension.

* TBAc has been determined to be a carcinogen and is under active review for delisting in SCAQMD.

ZemaSol is the only replacement for Xylenes and Toluene that is zero-VOC, low in toxicity, and mimics the physicochemical properties of the solvents. ZemaSol can be used across a wide variety of coatings, ink and adhesive resin systems.

KradaSol™

KradaSol was formulated as a dissolution solvent for various polymers and resins, as well as a primary or co-solvent in cleaning, paints, coats, inks and adhesives, to be used as a replacement for Hexanes and other solvents that are commonly used in these applications.

The following table documents the environmental, safety and performance considerations when comparing KradaSol to Hexanes.

	KradaSol	**Hexanes**
Environmental		
VOC Content: US EPA (outside SCAQMD)	**0**	100%

VOC Content: SCAQMD	**2.2* g/L**	100%
MIR (g O_3 / g organics)	**0.062**	1.45
Safety		
Exposure Limit	**> 200 ppm (OSHA PEL)**	50 ppm (ACGIH TLV)
Flash point (°C)	**20.7 (69.3 °F)**	-26 (-15 °F)
Physical Properties		
Kauri Butanol (Kb) **Value**	**49.2**	30

*ASTM Test Method 313-91. South Coast Air Quality Management District (SCAQMD) considers <5 g/L VOC content to be "zero VOC". KradaSol is 100% comprised of solvents considered to be VOC-exempt by the EPA, CEPA, NPRI and SCAQMD and as such is considered zero VOC.

KradaSol is comprised solely of VOC-exempt materials as determined by the EPA and SCAQMD, while Hexanes are VOC emitters in all jurisdictions. Furthermore, the MIR value for KradaSol is over 20 times lower than the MIR value for Hexanes.

The smallest component of KradaSol is the only component that has an OSHA/ACGIH maximum allowable exposure, at 200 ppm. Hexanes have a Threshold Limit Value (TLV) dictated by the ACGIH at a value of 50 ppm. The flash point of KradaSol is approximately 20.7 °C, which is significantly higher than the highly flammable Hexanes at -26°C. KradaSol presents a lower flammability risk and a better safety profile than Hexanes.

Additionally, the Kauri Butanol values demonstrate that KradaSol has greater solvency than Hexanes and can perform more efficiently as a dissolution agent.

In addition to the replacement of Hexanes, KradaSol can also be used to replace Xylenes, Toluene, Cyclohexane Perchloroethylene (Perc) and Methyl Amyl Ketone (MAK), and the physical properties of these solvents will be compared to those of KradaSol in the table below.

	KradaSol	Xylene	Toluene	Cyclohexane	Perc	MAK
Physical Properties						
Evaporation Rate (n-Butyl Acetate = 1)	**1.4**	0.7	1.6	0.4	2.1	0.4
Viscosity (cP)	**0.69**	0.81	0.55	1	0.89	0.81
Hansen Solubility Parameters $(MPa)^{1/2}$	**14.9**	17.9	18.2	16.8	19.3	17.6
Dispersion (δ_D)	**13.5**	17.6	18.0	16.8	18.4	16.2
Polarity (δ_P)	**5.7**	1.0	1.4	0	5.7	5.7
Hydrogen Bonding (δ_H)	**3.1**	3.1	2.0	0.2	0	4.1

KradaSol has a comparable evaporation rate to Xylenes, Toluene and Perchloroethylene. KradaSol also has similar viscosity and solubility profiles compared to Xylenes, Toluene, Cyclohexane, Perc and MAK.

KradaSol is the only zero-VOC solvent with an excellent toxicity, environmental, and performance profile for use as a dissolution solvent as well as many other applications.

BerdeSol™

BerdeSol was designed to act as a replacement for Heptanes for use in cleaning applications. The following table documents the environmental, safety and physical properties of BerdeSol compared to Heptanes.

	BerdeSol	**Heptanes**
Environmental		
VOC Content: US EPA (outside SCAQMD)	**0**	100%
VOC Content: SCAQMD	**0.9* g/L**	100%
MIR (g O_3 / g organics)	**0.047**	1.28
Safety		
Acute Toxicity (Oral LD_{50}, rat, mg/kg)	**> 5000**	> 5000
Flash point (°C)	**5.4 (41.7 °F)**	-4 (25 °F)
Physical Properties		
Evaporation Rate (n-Butyl Acetate = 1)	**2.5**	3
Surface Tension (dynes/cm)	**20.4**	20.1
Kauri Butanol (Kb) **Value**	**51.3**	29

*ASTM Test Method 313-91. South Coast Air Quality Management District (SCAQMD) considers <5 g/L VOC content to be "zero VOC". BerdeSol is 100% comprised of solvents considered to be VOC-exempt by the EPA, CEPA, NPRI and SCAQMD and as such is considered zero VOC.

BerdeSol is considered zero-VOC in the EPA and SCAQMD while Heptanes are VOC emitters in all jurisdictions. The MIR value for Heptanes is also over 20 times greater than the MIR value for BerdeSol, which signifies that BerdeSol has much less reactive potential for the formation of ground-level ozone and smog precursors.

The acute oral LD_{50} for Heptanes is comparable to that of BerdeSol. The flash point of BerdeSol is higher than the flash point of Heptanes, which makes BerdeSol a less flammable and safer product.

With respect to physical properties, BerdeSol has similar evaporation rate and surface tension compared to Heptanes, which allow for ease in solvent replacement. Furthermore, the solvency for BerdeSol is greater than Heptanes, and is thus more efficient at solubilizing certain compounds.

BerdeSol is an effective zero-VOC solvent replacement for Heptanes for use in various cleaning applications that has an enhanced safety and environmental profile, and has similar performance capabilities as Heptanes.

Conclusion

Six new solvent formulations developed by TBF Environmental Inc. have been described that provide more environmentally friendly and less toxic alternatives to solvents that are currently being used. The environmental and toxicity profiles, along with the physical parameters and performance characteristics, were compared to traditional solvents and have been proven to be suitable replacements in a variety of applications.

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