

D-LIMONENE USES AND INDUSTRIES

STRAIGHT SOLVENT REPLACEMENT

d-Limonene is an effective solvent to directly replace the toxic solvent components in existing solvent blends. One example is the 1:1 substitution of d-Limonene in the place of xylene or 1,1,1 tri-chlor in blends with other inexpensive solvents to make up the balance (mineral spirits, isopropylalcohol, butyl cellosolve, etc.). So long as no water is present, re-formulating may not be necessary in a strictly solvent-based system.

GENERAL PURPOSE CLEANERS

Aqueous systems incorporating d-Limonene, surfactants, and water are especially popular for economic and environmental benefits. Levels of 3%-7% d-Limonene with surfactants (ethoxylated alcohols, glycol ethers, ethoxylated amines) are common for all-purpose cleaners. Generally these formulas take a 2:1 ratio to emulsify d-Limonene at these levels (e.g. 10% d-Limonene, 5% surfactants, balance water). The addition of EDTA (chelates) to tie up metals, and phosphates (builders) such as STPP, TKPP, and metasilicates will contribute to the balance of the emulsion and probably significantly improve the overall effectiveness of the cleaner. These various ingredients can be adjusted to raise the pH to the desired level and improve chances of creating a stable "non-separating" formula. The 3%-7% d-Limonene level is effective on medium weight grease, oil, carbon and road film. It is an excellent whitewall tire cleaner in the concentrate form.

CLEANER FOR CONCRETE

d-Limonene has been used as a maintenance cleaner for concrete pads, parking complexes, and airport runways. The oils and greases that drip from cars can be lifted off the concrete either with a straight d-Limonene or a water diluted product. With straight d-Limonene, the product is put on the oil spots, which lifts the oil from the surface, and can be absorbed with a solid media such as kitty litter or oil absorptive pads. When using a water diluted product, use the traditional mop-and-bucket method. Some d-Limonene/water products have also been used in small floor scrubbers for removing oil and fork lift tire marks, and in larger units for taking up tire marks on runways.

d-Limonene will usually clean graffiti (including effectively replacing xylene in graffiti removers) off concrete because of its ability to remove paint. The effectiveness of graffiti cleaning products can also be enhanced by combining n-methyl pyrrolidone(NMP) with d-Limonene in a formulation. Strong enamels and epoxy paints will not usually be removed. State highway departments use d-Limonene to remove asphalt and tar from cement bridges. d-Limonene is not effective in other applications more suited for tile cleaners, toilet bowl cleaners, or areas where metal stains and mildew removal are necessary. d-Limonene is not effective in cleaning concrete from trucks (a job more suited for acids).

RELEASE AGENT

d-Limonene can be used at various levels for a release agent that is sprayed on the beds of asphalt trucks before picking up their loads to facilitate easy unloading. In the release agent application, d-Limonene may be a good replacement for diesel fuels commonly used in this application that are less suited to be dumped on the ground. Since d-Limonene will not readily freeze (-142° F freezing point), the product lends itself to underground storage through cold winters.

CIRCUIT BOARD CLEANING (Replacing CFC'S)

Regular grades of d-Limonene can be used alone for flux removal on circuit boards, but the d-Limonene may leave a slight film and does not flash off quickly. It can be used in combination with the other solvents to reduce CFC's or used straight when followed by an acetone or isopropyl alcohol rinse. High purity/low residue grades of d-Limonene are being introduced for PCB applications with some success, though cost of this material may be twice that of regular d-Limonene.

GREASE TRAP MAINTAINER

d-Limonene helps dissolve grease (butter, cooking oils, meat fat, etc.) and keeps foul odors down in restaurant grease traps. Recommended formulations contain mostly d-Limonene with a small percent nonionic surfactant for partial emulsification (e.g. 90% d-Limonene and balance E-Z-Mulse™). Since d-Limonene is an oil, it will float on top of the water in the grease trap catch basin. Local government regulations will dictate percent solids and solvent that can go down a drain.

PARTS WASHERS AND DIP BATHS

In the typically parts washer founded in most truck and automobile maintenance and repair facilities, straight d-Limonene can be used as a replacement for petroleum derived products. Aside from the health benefits to the workers from working with a much less toxic solvent, d-Limonene has proven to be a more effective cleaner. As with any organic solvent in this type of application, gloves should be worn to protect against skin dryness and irritation.

d-Limonene concentrates (e.g. 95% d-Limonene and 5% emulsifier) work well in closed automatic parts wash machines. The machines will dilute the concentrate automatically according to the quantity of water used in the wash cycle. Water-based concentrates do not work as well in this application because of a tendency to generate too much foam. Formulas should contain low foam or no foam surfactants (d-Limonene by itself depresses foam). An important caution -- hot soak tanks in areas of inadequate ventilation may cause workers to become nauseated by vapors and cause flash point concerns with concentrated fumes. Effluent from washer systems usually goes to holding tanks where local regulators can decide what can go down the drain and what should be hauled away for proper disposal.

SPOT AND STAIN REMOVERS

The trick to successful spot and stain removal is to first evaluate the type of stain and then select the correct cleaning agent. d-Limonene concentrates (95% d-Limonene, 5% emulsifier) can effectively remove ink, oil, grease, paint, tar, bubble gum, and asphalt. After the spot has been wet with the cleaner, a water damp rag should be used to rinse the product from the area. Blood stains, on the other hand, may require enzyme products. Rust, coffee and tea stains probably require low concentrations of mild acids (citric or phosphoric acid at 3-5%).

HAND CLEANERS

D-Limonene is very effective removing almost any soil including: ink, paint, grease, and tar. Solvent based hand cleaners usually contain approximately 30% solvent. At 10%, d-Limonene will out-perform most other solvent hand cleaners. Also the 10% level keeps cost competitive with traditional solvent-based systems. Generally, formulas require an equal percentage of surfactants to produce stable gel or lotion products. The addition of low levels of lanolin, jojoba oil, glycerin, or petrolatum reduces skin irritation associated with prolonged skin contact with d-Limonene. Many types of grit (gentle abrasives) besides pumice are sometimes added to heavy duty d-Limonene hand cleaners, including polyethylene beads and corn-cob grit.

CLEANER FOR PRINTING INKS

This is an area where d-Limonene is currently having mixed success. Even though d-Limonene is excellent at cleaning and removing ink from rollers and presses, it sometimes may not be cost effective against straight cheap solvent systems, but if used properly and in the right formulation it can be more effective and approach economic equality with less expensive systems. For most oil and solvent based inks, it is recommended that you use straight d-Limonene. It will clean the ink from the rollers faster and with less solvent use than with a petroleum product. Drying time and the interval between cleaning and running are about the same. Some inks, especially the water and soy based, can easily be cleaned with a 20-25% solution of d-Limonene in water. Care must be taken when formulating these types of products to ensure the surfactants used for emulsification can be rinsed off the rollers. Generally, a mixture of 20-25% d-Limonene, 5-7% emulsifier (like an ethoxylated alcohol), and 4% of a rinsing agent such as Dowanol TPM works well. It should be noted that most rubber rollers can swell when in contact with d-Limonene for extended periods of time, so exposure of the rollers to the cleaner should be kept to a minimum.

AEROSOL INGREDIENT

d-Limonene can combine nicely with other aerosol dispenser propellants to impart a pleasant citrus odor. d-Limonene in aerosols can directly replace III tri-chlor, xylene, and other undesirable solvents included in sprays for cleaning and degreasing. d-Limonene does not evaporate quite as fast as some other solvents and may leave a trace film, so some critical applications such as electronics cleaning will have to consider the product cautiously. Caution – always do stability work with d-Limonene when evaluating proper packaging. d-Limonene may attack gaskets and valves of some conventional dispensers. Viton and neoprene may be some of the best choices for aerosol stem gaskets (better than butyl or buna). Valves and cans should have an epon (epoxy) coating. Aerosol packagers and gasket suppliers should be consulted on materials recommended for d-Limonene.

PENETRATING OIL

d-Limonene can be used as a spray on product to loosen bolts and nuts, much like WD-40™. d-Limonene has the ability to wick into tight joints and dissolve hardened greases and oils to assist in the removal of bound nuts and bolts.

ADHESIVE REMOVAL

d-Limonene is a very good solvent for removal of adhesives from various substrates. Most contact adhesives will dissolve very quickly; however, d-Limonene has almost no effect on epoxies which have already cured.

MARINE VESSEL CLEANING

d-Limonene applications include degreasing diesel engines and bearings, removal of heavy carbon deposits, cleaning of slop hoses, cleaning and recycling of oil filters for extended life, and general-duty ship maintenance. d-Limonene should not interfere with oil and water separator sensor systems and is effective in oil water separators on large shipping vessels since d-Limonene and water separate so quickly. Additionally, d-Limonene has environmental advantages compared to other solvent-based systems.

A concentration of 20 to 25% d-Limonene, 15% miscellaneous surfactants and other desired actives, and balance water. The full strength concentrate can be employed in 24 hour dips to remove heavy carbon deposits on engine parts and valves. The cleaner can be reused for a number of applications. Various dilutions of the concentrate can perform various other useful jobs:

1:10 dilution to clean oily water separator filters

1:20 dilution for slop hoses (to adequately clean slop hose so it can be reused)
1:50 dilution for general purpose cleaning around the ship

SOLVENT CARRIERS

Most paint and adhesive formulations use some sort of carrier solvent to disperse the product over the intended area. In many cases d-Limonene can be used as the carrier instead of mineral spirits or other petroleum based compounds, often with a resulting reduction in the volume of solvent used. The drying times are generally not affected.

ASPHALT GRADING

d-Limonene has been approved as a solvent for use in asphalt grading. When asphalt is being laid, every so many pounds must be tested to insure that the proper mix of aggregate sizes and oils are being used. d-Limonene is very effective in the asphalt extraction methodology and has been approved by most highway departments.

Comparative Strength (Solvency) of Industrial Solvents Higher Values = Higher Dissolving Power

KB	VALUE	NOTES
Methylene Chloride	136	1, 3, 4
Trichlorethylene	129	1, 3, 4
Benzene	107	1, 2, 3, 4
Xylene	98	1, 2, 3, 4
Perchloroethylene	92	3, 4
D-Limonene	67	
Mineral Spirits	37	4
Naphtha	34	2, 3, 4
Kerosene	34	4
Stoddard Solvent	33	2, 3, 4
MEK	N/A	1, 2, 3, 4
Acetone	N/A	2, 3, 4

NOTES KEY

1 = Carcinogenic 2 = Flammable 3 = Toxic 4 = Non-biodegradable

MISCELLANEOUS NOTES

Generally, any oil and water system is called an "emulsion." Clarity (particle size) determines whether system is a micro or macro emulsion:

Micro emulsion: Clear emulsion of super-fine suspended oil particles in water (particle size .01-.1 microns).

Macro emulsion: Blue-White to milky-white emulsion of larger suspended oil particles in water (particle size .01-1 microns for blue-white emulsion, milky-white emulsion over 2 microns).

It is important to find the critical concentration of blend, so that mixture is not overloaded, causing frustrating stability problems. Experimentation is important since emulsion technology is both an art and a science.

It is hard to get freeze/thaw stable emulsions. Consequently, the formulator should conduct cloud-point testing and temperature-stability testing.

Solvents in general tend to lose their efficiency under high dilution rates compared to blended surfactant systems such as the combination of quat (a material which contributes to cleaning, kills germs, enhances nonionic), amine oxide (a grease cutter that helps keep solids in suspension), and a nonionic surfactant. Consequently, it is best to combine d-Limonene in these systems to provide the cutting ability (d-Limonene) and emulsifying properties (surfactants) to create a very effective formula for almost any job.

The most common nonionic surfactant currently used in the cleaning industry is probably NP9 (9 mole nonyl phenol). As an alternative to NP9, LA9 (9 mole linear alcohol ethoxylate) may be employed successfully. There is less biodegradability concern from LA9 since it degrades without forming unwanted benzene by-products associated with NP9.

In water-based concentrates, thickening can be obtained by the addition of NaCl (salt) or by changing the mixing procedure. Care must be taken not to throw off the HLB hydrophilic/lipophilic balance (water-loving/oil-loving balance) on delicate systems. This can cause "cloudiness" or separation.

A common concern in formulating with d-Limonene is how to get an easy stable, "nonseparating," clear emulsion. One way is trial and error with surfactant blends. There are many good surfactants on the market which, when used in adequate levels with d-Limonene as the only solvent, form very stable emulsions. Another way (if your application can tolerate a "non-natural" ingredient) is to add butyl cellosolve, EB, or some other solvent at various levels to stabilize the system.

Mixing procedure is important to avoid jelling. When mixing water-based d-Limonene concentrates, slowly add the oil phase mixture to the water phase mixture. An example would be the addition of the oil phase mixture of d-Limonene and ethoxylated amine to the water phase mixture of the water, NP9, quat, amine oxide, and EDTA.

Corrosion should not be a problem with most d-Limonene water base cleaners, especially when formulas employ ethoxylated amines that plate out on metal surfaces to help avoid flash rusting.

Miscibility of d-Limonene with other solvents

Benzyl Benzoate, Diethyl Phthalate	Complete
Turpentine, Acetone, Petroleum Ether	Complete
Gasoline, Mineral Spirits, Benzene	Complete
Toluene, Xylene, d-Limonene, dipentene	Complete
Chloroform, Carbon Tetrachloride	Complete
Ether, Ethylene Glycol, n-Butyl Propionate,	Complete
Methyl Alcohol, Ethyl Alcohol, Butyl Alcohol, Isopropyl alcohol, Amyl Acetate, Amyl Alcohol	Complete
Glycerin	Very slightly soluble
Propylene Glycol	Insoluble

MISCIBILITY OF D-LIMONENE WITH DRYING OILS

Linseed Oil, raw or boiled, Tung Oil, Fish Oil, Corn Oil, Esterfied Tall Oil	Complete
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NON-SOLVENT APPLICATIONS FOR d-LIMONENE

CHEMICAL SYNTHESIS

d-Limonene is an interesting organic molecule to synthesize other compounds. Current commercial applications include production of tackifying terpene resins used in such diverse applications as adhesives for disposable baby diapers and floor coverings, and production of L-carvone, the imitation spearmint flavor used in many brands of tooth paste.

PESTICIDE APPLICATIONS

d-Limonene can effectively kill ants, termites, and other insects on contact. Several popular flea dips for dogs and cats incorporate d-Limonene. Unfortunately, there is not a generic EPA registration for d-Limonene at this time, so users must individually go through cumbersome and expensive registration process to legally market d-Limonene in bug-killer applications. d-Limonene can be an inert wetting agent in oil-based pesticides.

MEDICAL RESEARCH

Researchers at the University of Wisconsin and other institutions are studying the anti-cancer properties of d-Limonene, targeting potential applications to fight breast cancer in humans.

ODORANT

d-Limonene has been used by the petroleum industry for years to make mercaptans for natural gas markers. The pleasant citrus aroma of d-Limonene can be incorporated into room air-fresheners, automobile air-fresheners, etc.

EXTENDER

Flavor and fragrance industry uses fairly large quantities of d-Limonene to extend other more valuable natural oils.