A DLI White Paper:

Key information on industry solvents

July 2007

Over the past several years, the Drycleaning and Laundry Institute (formerly IFI) has included a solvent comparison table in presentations on the industry's future. Looking at the limitations of those presentations and the industry's need for guidance, DLI has prepared this review and evaluation of current industry solvents for its members. The information presented here is accurate to the best of our knowledge as of July 2007. The review and evaluation is just that, and does not constitute an endorsement of any individual solvent. In summary, our intent was to provide what we believe is the critical information that would be used by a member in coming to a decision on whether to use a particular solvent.

In looking at DLI's overview and evaluation of each solvent, keep in mind that while we addressed major regulatory concerns at the federal level, there will be variations at the state level. For that reason, DLI urges anyone making a decision on using a new solvent to check with the department of environmental protection for their state, and to also check with their fire marshal regarding local and state fire codes. Finally, DLI recommends that all plants consider disposing of their waste with a local hazardous waste hauler.

In addition to regulatory issues, there are almost universal concerns by landlords over the possibility of solvent contamination. In turn, these concerns have led to prohibitions on the use of certain solvents, or even to a prohibition on the use of any solvent system whatsoever. For those reasons, DLI strongly recommends that anyone considering a new solvent discuss that system with their landlord before signing a lease, or before making a decision to purchase new equipment.

The Drycleaning and Laundry Institute is providing this white paper as a service to its members and by extension to the industry as a whole. We hope members feel we have met our goal of providing sufficient information and guidance on each solvent so that a truly informed decision can be made.

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A. Perchloroethylene

History/background: Perchloroethylene (perc) is the oldest synthetic solvent used in the drycleaning industry. Although carbon tetrachloride was the first synthetic, non-flammable solvent, it was quickly replaced by perc because of its toxicity and because it caused corrosion damage from acid formation when it contained even small amounts of moisture. Use of perc began in the late ’40s and early ’50s, and by 1960 had surpassed Stoddard as the primary solvent used by drycleaners in the United States.

Operational considerations: More work has been done developing perc drycleaning equipment and detergent systems than with any other solvent, and the modern day perc system arguably continues to give the best overall cleaning results of any solvent. Because of its high solvency, however, perc is not the best choice for solvent-sensitive items. A compete drycleaning cycle for a typical load averages 30 to 35 minutes. With today’s fourth and fifth generation machines, losses to the atmosphere average four fl. oz per day, or about 0.42 pounds per day.

Regulatory considerations: DLI believes that the best evidence indicates that perc is unlikely to be a human carcinogen, and that it is unlikely to contribute to neurological or developmental problems. As there is no absolute certainty, however, the institute’s recommendation since 1977 has been that the industry must continue to reduce exposures and emissions pending these issues being resolved.

Under U.S. EPA’s National Emissions Standards for Hazardous Air Pollutants (NESHAP), perc is regulated as a hazardous air pollutant. At this time, EPA has published an extension to the NESHAP which phases out perc operations in co-residential locations, although this is under court challenge. The state of California has enacted a phase-out on all perc drycleaning over the next 15 years, culminating in a ban in 2023, and New Jersey and Massachusetts have also been giving consideration to a phase-out. In contrast, both North Carolina and Oregon have done their own extensive reviews of perc and feel that perc is unlikely to be a human carcinogen, and that additional regulations or bans are unnecessary. Perc is classified as a hazardous waste and must be disposed of as such, and levels have been set for it under U.S. EPA’s Drinking Water regulations. Finally, perc is not a volatile organic compound (VOC) contributing to smog formation, it is not a stratospheric ozone depletor, and it is not a green house gas.

DLI’s evaluation: We believe that perc is used responsibly by most drycleaning plants and it continues to be one of the safest solvents in use in

the industry. Unfortunately, previous disposal practices (while legal at the time) have resulted in soil and groundwater contamination at some locations. Concerns about potential liability for contamination have resulted in many landlords refusing to permit a perc operation on their property.

While we believe that the best available evidence indicates that perc is unlikely to be either a human carcinogen or cause nervous system disorders, these issues have led to ongoing regulatory actions (including a state-wide ban in California), which in turn have fueled intense media scrutiny.

In light of the regulatory/political issues and media scrutiny of perc, DLI believes that a member considering an investment in a new drycleaning system would be best advised to first consider alternative solvents, and to evaluate them against the difficulties of using perc today.

B. Petroleum and hydrocarbon solvent systems

History/background: Petroleum solvents such as Stoddard are the oldest solvents in use in drycleaning and have been available since the late 1920s. Prior to the introduction of Stoddard solvent (which DLI helped develop, and which was named after former DLI President W.J. "Dixie" Stoddard), gasoline was the only solvent generally in use, and fire losses, in 1925 dollars, were running in the range of $400 million dollars or more each year. The past decade has seen the introduction of modern hydrocarbon solvents which can be used in the same drycleaning equipment as petroleum solvents.

Operational considerations: Petroleum and hydrocarbon solvents are combustible — that is, if the solvent is heated sufficiently, a flash point is reached where the vapors coming off that solvent will ignite in the presence of a spark or a flame. Because of this characteristic, varying levels of explosion-proof controls are required for petroleum/hydrocarbon equipment.

With their lower solvency power, petroleum and hydrocarbon solvents are safer for solvent-sensitive items such as decorative beads, garments with plasticizers, and garments susceptible to dye bleeding.

Because of the lengthy drying cycle needed with these solvents (typically a minimum of 30 minutes), the cleaning and drying cycles may total one hour or more. As a result, the throughput in a machine of a given capacity will usually be considerably less than for a perc system of the same capacity. Members considering a switch from perc to petroleum or hydrocarbon solvents should give careful consideration to this factor when deciding on the wheel capacity that will be needed in their equipment.

Regulatory considerations: Various classes of petroleum and hydrocarbon

solvents have different flash points; solvents with higher flash points can be used in machines with fewer explosion-proof controls. Fire codes in major jurisdictions may prohibit the use of lower flash point classes, while allowing higher flash point solvents.

Petroleum and hydrocarbon solvents are regulated under U.S. EPA's New Source Performance Standards (NSPS) as volatile organic compounds (VOCs) — that is, as solvents that contribute to smog formation. At this time, California is the only jurisdiction that has given even a preliminary indication of the possibility of further future regulation of these solvents as contributors to smog formation.

Under the U.S. EPA's hazardous waste regulations, solid waste (such as cartridge filters) from petroleum/hydrocarbon systems would not be considered a hazardous waste, but liquid waste (such as still residue) would be a hazardous waste unless it had a flash point above 140°F.

DLI's evaluation: With its ability to safely clean most solvent-sensitive items, almost any garment can be done safely in petroleum or hydrocarbon solvents. Additionally, a wide variety of detergent and additive systems exists for these solvents. Today's advanced dry-to-dry cleaning systems have excellent solvent mileage and are comparable to perc systems in this respect. Because petroleum/hydrocarbon vapors can form explosive mixtures in air, controls to deal with this must be incorporated in dry-to-dry systems. Controls which act to prevent an explosion would generally be preferable to those which are designed to put out the fire after an explosion occurs.

Given the many positives, petroleum or hydrocarbon solvents make excellent choices for a cleaning system as long as adequate consideration is given to the reduced throughput for a machine of a given load capacity when compared to perc, and as long as local fire codes will not pose any problem. A final consideration is that a higher level of solvent maintenance is critical to prevent the buildup of odor-causing bacteria.

C. Greenearth

History/background: Less than 10 years old, GreenEarth is one of the newer drycleaning systems now available. The solvent in a GreenEarth system is based on silicone chemistry. The particular siloxane used in GreenEarth (D5 or decamethylcyclopentasiloxane) is also used in cosmetic and related preparations. GreenEarth systems are sold under license, and the current licensing fee is $2,500/year for the first machine.

Operational considerations: While GreenEarth is considered as combustible, it has a relatively high flash point of 170°F. Because of its lower solvency

power, GreenEarth — similar to petroleum/ hydrocarbon solvents — is safer for solvent-sensitive items such as decorative beads, garments with plasticizers, and garments susceptible to dye bleeding.

In the IFI Fellowship bulletin on GreenEarth (No. F-47, September 2002), we found an average overall cycle length of 53 to 58 minutes. As with hydrocarbons, members considering a switch from perc to GreenEarth should give careful consideration to this factor when deciding on the capacity of the machine they need to purchase.

Regulatory considerations: GreenEarth must be used in a Class III A drycleaning machine. Fire codes in major jurisdictions will pose few if any problems, but members are advised to confirm this before moving forward.

As long-term exposure studies were done in animals, one study in rats indicated an increase in a certain type of tumor. Siloxane manufacturers have conducted further studies and have concluded that the tumor mechanism in rats is not applicable to humans. The results of these studies have been submitted to California EPA and U.S. EPA, and are currently being reviewed.

One key consideration is that GreenEarth is not regulated as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) or as a "hazardous substance" under Superfund. GreenEarth Cleaning recommends that a licensed hazardous waste hauler handle it, but as a non-hazardous waste. Finally, GreenEarth is not a stratospheric ozone depleter, and is designated by U.S. EPA as not being a volatile organic compound (VOC).

DLI's evaluation: GreenEarth Cleaning commissioned an exhaustive IFI Fellowship study of the GreenEarth system, in which everything from flammability to stain removal to operating costs was evaluated. With the particular detergent provided by GreenEarth for the final testing, IFI found that "…GreenEarth was a viable alternative to perc drycleaning." Operating costs — which included the license fee — were slightly higher than that for a perc system. DLI members can request a copy of the full Fellowship from GreenEarth Cleaning or DLI. As with petroleum and hydrocarbon solvents, GreenEarth has the ability to safely clean most solvent-sensitive articles, and almost any garment can be done safely in it.

D. Carbon dioxide and Solvair systems

History/background: The first carbon dioxide (CO_2) cleaning systems were introduced in February 1999 by Micell Technologies, Inc.; these systems use extremely high pressure (around 600 psi) so that the CO_2 is in liquid form. According to knowledgeable sources, there are approximately 40 to 50 CO_2 retail drycleaning systems operating in the U.S. today. We know of no U.S.

manufacturers of CO2 drycleaning machines at this time, but we understand that the Chinese manufacturer SailStar is offering a machine in the U.S.

Solvair is a new process introduced by R.R. Street & Co. Inc. in July 2006, with the first machines scheduled for installation in summer 2007. The Solvair system is a hybrid system, using what DLI understands is a glycol ether solvent for the cleaning cycle, which is subsequently extracted from garments by CO2 after the cleaning cycle is completed. As a result, CO2 is the only atmospheric release from the system.

Operational considerations: A drycleaning machine using liquefied carbon dioxide operates at pressure levels as high as 400 psi to 600 psi. Because of those levels, the machines are classified as high-pressure vessels, and consequently have been expensive — typically well over $100,000, with Micell machines at more than $150,000. As of summer 2007, R.R. Street is quoting $150,000 for their Solvair Cleaning System.

Because solvency is very low, spotting requirements for a traditional CO2 system can be considerably higher than with other solvents. In the Solvair system, the initial glycol ether solvent has an extremely high solubility for water (up to 12 percent) and detergents and other additives can be used effectively, something that is not true of regular CO2 systems. As a result, soil removal and stain removal during the cleaning process appear to be significantly improved when compared to CO2 systems up to this point.

A regular CO2 system goes through a cleaning cycle, extraction, and a final pump-out of the CO2. The Solvair system goes through a cleaning cycle using glycol ether, followed by extraction, and multiple rinses with CO2 to remove the glycol ether, followed by a final pump out of the CO2. Both systems then have approximately six pounds of CO2 left in the wheel when the cylinder is depressurized. The one to two minutes it takes to depressurize the cylinder makes up the entire drying cycle for a CO2 machine. Because effectively no time is needed for the drying cycle, CO2 systems typically have a total cycle of 30 minutes or less.

Regulatory considerations: Because liquefied CO2 under high pressure will immediately flash off if there is any type of leak in the machine, no CO2 could reach the ground, much less cause soil or water contamination. There are no regulations on liquefied CO2 as a drycleaning solvent, either at the federal level or the state level. Note, however, that California may at some time evaluate the small release of CO2 at the end of the drycleaning cycle due to greenhouse gas concerns. Is this likely to be significant? DLI recently researched figures from the American Council for an Energy Efficient Economy, which rated the best (lowest CO2 emissions) autos as the Toyota

Prius and the Honda Civic Hybrid, at five tons and six tons per year, respectively. DLI has calculated that a CO2 machine using six pounds of CO2 per load would be equivalent to one Honda Civic each year. Based on our calculation, even if most of the industry converted to CO2 cleaning, the contribution to global warming would be negligible.

DLI's evaluation: Regular liquefied CO2 systems are very expensive and have fairly low cleaning ability, but they are one of the "greenest" systems ever used in drycleaning. For a number of cleaners, the greenness of the system has offset the lackluster cleaning and high costs. The newly introduced Solvair system appears to overcome the lack of cleaning performance, and does so while maintaining the virtue of a very short overall cycle. At this time, a CO2 or Solvair system can be installed virtually anywhere in the U.S. without any real concerns.

Finally, Solvair is being sold as a cradle-to-grave system, and R.R. Street & Co. Inc. will be providing not only the solvents and additives, but will be arranging for proper waste disposal as well.

E. Drysolv (n-propyl bromide, or 1-bromopropane)

History/background: n-propyl bromide (NPB) is a crossover solvent from metal degreasing and was first introduced by current vendors last year for drycleaning purposes.

Operational considerations: Stabilized n-propyl bromide is being offered to the industry under the trade name DrySolv and is being marketed as a drop-in replacement for perchloroethylene.

Based on Enviro Tech International's February 28, 2006, Material Safety Data Sheet (MSDS) for DrySolv (available on the Enviro Tech website) many of the handling considerations are similar or identical to those for perc. For example, the MSDS states, "High concentrations are irritating to the respiratory tract and may cause headache, dizziness…or narcosis. Chronic overexposure at high levels many cause adverse effects in the central nervous system, reproductive system, respiratory system, kidney, and liver."

As with perc, the MSDS for DrySolv states that open flames, electric arcs, and similar should be avoided since thermal decomposition will produce carbon monoxide, carbon dioxide, and hydrogen bromide.

According to the Enviro Tech MSDS, DrySolv does not have a flash point. Other MSDS's for pure NPB state the flash point is 70−77°F. To resolve this significant issue, DLI has done its own testing with both open and closed cup flash point methods. In our testing we reached 200°F and found no flash

point. We have also reviewed the Factory Mutual report posted on the Enviro Tech website, and in subsequent conversations with Factory Mutual, we learned that DLI and FM observed similar conditions with sputtering of the flame head because of the halogen content, but that no true flash point was observed by either of us.

While there is no flash point, the DrySolv MSDS states, "Flammable Limits: Estimated 3.8 to 9.5 percent by volume in air based on NPB." DLI does not know of any study measuring NPB concentrations during the drying cycle in a drycleaning process.

In its recent rule on NPB, EPA agrees that it does not have a flash point by standard test methods but that it does have upper and lower flammability limits—and if the concentration of vapor falls between the upper and lower flammability limits it could catch fire in presence of a flame. EPA then notes that "…users should take appropriate precautions in cases where the concentration of vapor could fall between the flammability limits."

Under "Conditions to Avoid," the MSDS states that "prolonged contact with free water may result in diminished stabilizer and corrosion." The issue here is that some chemicals, including some chlorine and bromine compounds, are subject to hydrolysis, where acids form in the presence of free water. An example of this is carbon tetrachloride, which is also subject to hydrolysis. In the 1940s, severe corrosion of equipment became a major problem for drycleaners using carbon tet. However, free water is less of an issue with today's detergent systems. According to information posted in a web forum by DrySolv representatives, Union (and, DLI now understands, Columbia as well) will not warranty a machine that has DrySolv in it, while Firbimatic (and possibly others) will warranty their machines for use with it. DLI urges members to heed the caution in the MSDS about avoiding the presence of free water in their system, and to consult with their machine manufacturers and solvent distributors.

Regulatory considerations: In May 2007, EPA published in the Federal Register its determination that NPB is acceptable for use as a substitute for ozone-depleting substances in metal cleaning, electronics cleaning, and precision cleaning applications. EPA based this determination on the Agency's conclusion that NPB exposures in the range of 17 to 30 ppm in such applications were not likely to have adverse human reproductive effects. (At the same time, EPA has proposed that NPB's use in aerosol or adhesive application would be unacceptable based on higher anticipated workplace exposures.) The state of California and the European Community require that NPB be labeled as a reproductive hazard.

In its Final Rule of May 30 approving the use of NPB for cleaning of metals, etc., EPA addresses a number of questions on NPB. In summary of EPA's information:

NPB may be controlled as a volatile organic compound (VOC) under state air plans developed to attain national standards for smog. DLI notes that members considering NPB should check to be certain their state does not regulate NPB as a VOC.

Available data indicate that NPB is less persistent in the environment than many solvents and would be of low to moderate concern for movement in soil, and that the toxicity to aquatic life is moderate, and that it would probably not be listed under the Toxics Release Inventory.

NPB is not currently regulated as a hazardous air pollutant, is not listed as a hazardous waste under RCRA, and is not required to be reported under the Toxic Release Inventory under the Superfund Amendments and Reauthorization Act (SARA). EPA notes, however, that large amounts of NPB might be hard to dispose of in water, therefore, users should not dump it into water, but dispose of it as they would a spent halogenated solvent.

In an extensive discussion of reproductive toxicity, EPA rejected the proposed ACGIH exposure level of 10 ppm, and concluded that concentrations which do not exceed the range of 18 to 30 ppm should be protective of health.

Finally, while NPB is not regulated as a hazardous waste, DrySolv representatives have noted that "…proper waste management is mandatory for this industry and we go to great lengths to support proper stewardship." DLI believes this is a responsible position.

DLI's evaluation: As DrySolv is marketed as a direct drop-in replacement for perc in Class IV machines, the increasing regulatory pressures (and phase-outs) on perc are certain to create additional interest in this solvent.

General cautions with respect to inhalation, skin contact, eye contact, etc. are virtually identical to perc. While not listed as a hazardous waste, IFI concurs with the DrySolv recommendation to use a hazardous waste hauler. The DrySolv MSDS notes that chronic overexposure at high levels may cause adverse effects to the reproductive system, and this is noted in EPA's Final Rule. This is one area that is significantly different from perc, which has been found to have no adverse effects on reproduction.

In summary, DrySolv — a stabilized NPB — is now available to the industry as a replacement for perc. Industry experience is relatively limited at this time. DLI recommends that members considering DrySolv carefully heed all

cautions and warnings in the MSDS, and that they discuss this and any other available information with distributors, manufacturers, and their state environmental department as part of their decision-making process.

F. Pure Dry

Pure Dry is a solvent introduced into the industry in 2000. Pure Dry is reportedly a hybrid solvent composed of hydrocarbons, hydrofluorethanes, and perfluorcarbons, with a flash point of approximately 350°F. Reportedly, the original blend had a base hydrocarbon solvent in it with a flash point of less than 100°F, and when other components were lost during distillation, the overall flash point dropped significantly. DLI's understanding is that Shell's hydrocarbon is now used in the blend as the base solvent and has a flash point well over 100°F. DLI has no direct information on operational or regulatory considerations, and we recommend that anyone considering Pure Dry should speak to members who have used the solvent and to their state environmental agency.

G. Rynex

Rynex was developed in the late 1990s as an alternative to perc, and in the patent is described as a "di-propylene glycol tertiary-buyl ether." Since Rynex had made the business decision to not do a Fellowship with DLI, we have very little direct information. There is still at least one Rynex distributor in Northern California, and members interested in the solvent may wish to contact them for product information.

H. Wetcleaning

DLI believes that wetcleaning is a valuable adjunct to solvent cleaning, and that it should be part of the garment care options available in any drycleaning plant. In the early 1990s, IFI (now DLI) founded the Professional Wetcleaning Partnership (PWCP), and was joined in this by the Center for Neighborhood Technology (the first wetcleaning demonstration site) and by Greenpeace.

History/background: PWCP actively promoted the use of wetcleaning in the drycleaning industry — and as a group recognized that 100 percent wetcleaning is not realistically feasible.

Operational consideration: IFI, the Center for Neighborhood Technology, and Greenpeace agreed on the use and economic feasibility of wetcleaning, as follows:

About 25 to 40 percent of the garments coming into a drycleaning plant should be able to be wetcleaned with no significant change in finishing requirements.

Up to 60 to 80 percent of the garments coming in could be wetcleaned, but tensioning finishing equipment is an absolute requirement, and costs will increase because of the additional labor needed for finishing.

Up to 90 percent and byond can be achieved, but this will require maximum effort and significant changes in plant practices leading to further increases in cost.

DLI notes that one of the foremost practitioners of wetcleaning in the U.S. eventually adopted a solvent cleaning system the owner/operator felt was environmentally acceptable. Following this change, the proportion of garments that were wetcleaned declined because of the higher labor costs, and a natural balance eventually came about which maximized the benefits of wetcleaning while minimizing the higher costs. That natural balance point — with no outside influences on the decision — was approximately 65 percent drycleaning and 35 percent wetcleaning.

3. Regulatory considerations: In many areas of the country, municipalities impose significant fees on the installation of new washing equipment because of the burden placed on sewer treatment facilities. Beyond that, there are few if any additional regulatory considerations involved with wetcleaning operations.

4. DLI's evaluation: DLI believes that wetcleaning is a valuable and necessary adjunct to solvent cleaning, and should be available in most, if not all, drycleaning plants. Once a plant begins to reach the 20 to 30 percent range in wetcleaning, it may wish to evaluate tensioning finishing equipment to recover shrinkage losses. If there were a wholesale shift to wetcleaning in an area or in a state, total water consumption and total sewer discharge would be likely to become issues, particularly in areas where there are already limitations on water supply.

In the 1970s and early 1980s, average 8-hour TWA's were 43 ppm. Today, 8-hour TWA's average about 12 ppm, a drop of about 72%.

The industry's consumption of perc has fallen by 88% since 1985, from 260 million lbs/year to 31 million lbs/year in 2005. More importantly, air emissions have decreased 98.7% since 1985.