Chemicals Used In Drycleaning Operations

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Chemicals Search Menu

The following resource was developed for the State Coalition for Remediation of Drycleaners (SCRD) using material safety data sheets (MSDS) and other sources. The report was prepared by Bill Linn, Florida Department of Environmental Protection (FDEP). Scott Stupak, North Carolina Superfund Section, provided technical support for database development.

INTRODUCTION

A wide variety of chemicals has been used and is currently utilized in drycleaning operations. Using material safety data sheets (MSDS) and other sources; a drycleaning chemical data base was developed that includes many of the chemicals that have been used in drycleaning operations. These data and the accompanying text are intended to aid those engaged in the assessment and remediation of contaminated drycleaning sites and to assist regulators conducting compliance inspections at drycleaning facilities. Some of the chemicals/products listed on the spreadsheet are no longer manufactured, marketed or used in drycleaning operations.

Drycleaning Chemical Data Spread Sheet

The spread sheet is divided into the following categories:

- Chemical product or trade name (as listed on the MSDS)
- Chemical manufacturer or distributor
- Use or function of the product
- Additional information
- Chemical constituent(s) as listed on the MSDS
- Chemical Abstract Numbers (CAS #s) for listed constituents
- Relative concentration of the constituent in the product

All product ingredients or constituents that appear on the MSDS were listed on the spread sheet – both hazardous and non-hazardous. The manner in which product constituents are reported on MSDS varies widely. Many manufacturers/vendors simply list all ingredients as being proprietary (trade secrets). Others indicate that there are hazardous constituents in the product, but do not identify the constituents. Some MSDS include statements to the effect that there are no hazardous

alkanes, 30 – 40% cycloalkanes, and 10 – 20 % alkyl aromatic compounds (Sciences International, 1995).

The high aromatic content petroleum solvents are no longer widely used in drycleaning (Schreiner, 2001). Since the introduction of Stoddard solvent, the industry trend has been towards the development of higher flash point petroleum drycleaning solvents which have little to no aromatic hydrocarbon content. In 1950, the National Institute of Cleaning and Dyeing worked with the U.S. Bureau of Standards to develop standards for a higher flash point petroleum drycleaning solvent known as 140-F solvent (Michelsen, 1957). Beginning in the early 1990s petroleum drycleaning solvents with even higher flash points were developed such as:

- **Drycleaning Fluid-2000 or DF-2000™ Fluid:** This solvent is manufactured by ExxonMobil Chemical Company and was first marketed by Exxon Chemicals in 1994. It is described as synthetic, hydro-treated aliphatic hydrocarbons. More specifically, it is composed of C_{11} to C_{13} hydrocarbons (isoparaffins and cycloparaffins). It contains no aromatic compounds. It has a flash point of 147° F.

- **EcoSolv® Dry Cleaning Fluid:** This solvent is manufactured by Chevron Phillips Chemical Company LP. It was originally marketed under the name of HC-DCF High Flash. It is described as a mixture of aliphatic hydrocarbons, but more specifically it is composed of a mixture of $C_{10} – C_{13}$ isoparaffins. It has a flash point of 142° - 144° F.

- **Hydroclene® Drycleaning Fluid:** This solvent is manufactured by Shell Chemical Company but is marketed by Caled Chemical. It "…is a mixture of normal-, iso- and cyclo-paraffins…" (CARB, 2005). It has a flash point of 145° F.

- **Shell Sol 140 HT:** This solvent is manufactured by Shell Chemical Company. It is mixture of predominantly $C_9 – C_{12}$ hydrocarbons. It has a flash point of 145° F.

One of the problems associated with petroleum drycleaning solvents is biodegradation. Bacteria introduced into the drycleaning system through the clothing or in water introduced into the system will feed on the petroleum solvent, detergents, oils and fatty acids producing "sour smells". To combat this problem, bactericides or antioxidants are added to the system, normally in detergents. The biocides used today are reportedly similar to those used in shampoos, laundry products and cosmetics. In the past, PCE was added to drycleaning soaps used with petroleum drycleaning solvents as a bacterial inhibitor (Albergo, 1997). Butylated hydroxytoluene (BHT), an anti-oxidant or oxygen stabilizer is added (10 ppm) to EcoSolv®, the high-flash petroleum drycleaning solvent manufactured by Chevron Phillips Chemical Company LP (CARB, 2005).

Two products currently marketed to inhibit biodegradation of petroleum drycleaning solvents include:

- Desolan NT: This product is manufactured by SEITZ GmbH Chemische Fabrik and is described as an odor eliminator. It contains an ingredient described as "bacteriostatics".

- Varnicide: This product is manufactured by Adco, Inc. It is described as an "antioxidant/microbial – to prevent the development of rancid odors."

Carbon Tetrachloride

Carbon tetrachloride was the first chlorinated solvent used in drycleaning operations. It was first imported to the United States from Germany by Ernest C. Klipstein in 1898 and was sold as a drycleaning and spot-removing agent under the trade name of Carbona (Doherty, 2000). It was commonly used in drycleaning by the 1930s. By 1940 annual carbon tetrachloride use by the U.S. drycleaning industry was estimated to be 45 million pounds versus 12 million pounds of Perchloroethylene and 5 million pounds of trichloroethylene (Michelsen, 1957). Carbon tetrachloride was sometimes blended with other solvents for use as a drycleaning solvent. Because of its high toxicity and tendency to contribute to machinery corrosion, carbon tetrachloride is no longer used in drycleaning operations. Carbon tetrachloride was phased out as a drycleaning solvent in the early 1950s (Kirk-Othmer, 1965).

Trichloroethylene

In 1930, trichloroethylene (TCE) was introduced as a drycleaning solvent in the United States (Martin, 1958). TCE causes bleeding of some acetate dyes at temperatures exceeding 75 degrees Fahrenheit. It was never widely used in this country as a primary drycleaning solvent. TCE is, however, still widely used as a dry-side pre-cleaning or spotting agent and in water repellent agents. TCE is the principle ingredient in Fast PR, 2-1 Formula, Picrin, Puro, SemiWet Spotter, Spra-Dri and Volatile Dry spotter (V.D.S.).

Perchloroethylene

The first commercial production of perchloroethylene (PCE) in the United States occurred in 1925 (U.S. E.P.A., 1989). However, the first documented use of PCE as a drycleaning solvent in the United States was in 1934 (Martin, 1958). The superior cleaning ability of PCE, coupled with some municipal fire codes prohibiting the use of petroleum solvents in drycleaning operations resulted in the increasing use of PCE in drycleaning operations. By 1948, perchloroethylene replaced carbon tetrachloride as the leading chlorinated solvent used in drycleaning (Chemical Week, 1957). In 1962, PCE became the drycleaning solvent of choice in the United States and drycleaning accounted for 90% of PCE consumption (Chemical Engineering News, 1963).

In general, there are four grades of manufactured PCE: a drycleaning grade, a vapor degreasing grade for metal degreasing, a technical grade for the manufacture of other chemicals and a high purity grade used for extraction. Drycleaning-grade PCE is produced in the United States by Dow Chemical (trade name DowPer™), Vulcan Chemicals (trade name PerSec®), and PPG Industries, Inc. Drycleaning-grade PCE is also produced by ICI (Ineos Chlor Americas) under the trade names Perklone™ D and Perklone™ DX, and exported to the United States.

Material Safety Data Sheets for drycleaning-grade PCE indicate that it has a purity ranging from 99% to 99.9%. Some of the documented impurities are: 1,1,1-trichloroethane, carbon tetrachloride, dicholoromethane, trichloroethylene, water and other chlorinated solvents (European Communities,

constituents in the product based on current regulations as they (the vendor/manufacturer) interpret them. Therefore, some of the products listed on the spreadsheet have no data listed for constituents. Some of the chemical manufacturers, however, do offer fairly comprehensive data on constituents in their MSDS.

Chemicals used in drycleaning operations can be grouped into five broad categories:

- Drycleaning Solvents
- Other Chemicals Used In the Drycleaning Machine
- Pre-cleaning/Spotting Agents
- Garment Treatment Chemicals
- Chemicals Used In Solvent & Equipment Maintenance

DRYCLEANING SOLVENTS

Historically, a number of different chemicals have been utilized as drycleaning solvents. These include: camphor oil, turpentine spirits, benzene, kerosene, white gasoline, petroleum solvents (primarily petroleum naphtha blends), chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, 1,1,2-trichlorotrifluoroethane, glycol ethers, 1,1,1-trichloroethane, decamethylcylcopentasiloxane, n-propyl bromide and liquid carbon dioxide.

Petroleum Drycleaning Solvents

Petroleum-based compounds have been the most widely used solvents in drycleaning. At the beginning of the twentieth century, raw white gasoline was the drycleaning solvent of choice in the United States. Because of fires and explosions associated with the use of gasoline, drycleaning facilities were unable to obtain insurance and many cities banned drycleaning operations within their city limits. Due to these circumstances, a drycleaner from Atlanta named William Joseph Stoddard worked with Lloyd E. Jackson of the Mellon Research Institute and the petroleum refining industry to develop a less volatile petroleum drycleaning solvent in 1924 which is now known as Stoddard solvent. In 1928, the U.S. Department of Commerce promulgated Commercial Standard CS3-28 which required that petroleum drycleaning solvents must have a minimum flash point of 100 degrees Fahrenheit. Drycleaners began using Stoddard solvent in 1928 (Martin, 1958). From the late 1920s until the late 1950s Stoddard solvent was the predominant drycleaning solvent in the United States.

Stoddard solvent is a mixture of petroleum distillate fractions (petroleum naphtha) which is composed of over 200 different compounds. These solvents are composed predominantly of alkanes and cycloalkanes, with some aromatic compounds. Although many people refer to any petroleum drycleaning solvent as Stoddard solvent, this is incorrect. More properly, Stoddard solvent is a mixture of $C_5 - C_{12}$ petroleum hydrocarbons containing 30 – 50% straight- and branched –chained

2005). Perchloroethylene is a highly oxidized compound and has been called the most stable of the chlorinated solvents. However, PCE degrades in the presence of light, heat and oxygen to form trichloroacetyl chloride and tetrachloroethylene oxide. If water is present hydrochloric acid is generated (Knight, 1969). Water is present in the drycleaning machine and distillation of spent solvent at high temperatures can result in PCE breakdown. The presence of impurities in PCE, such as 1,1,1-trichloroethane and trichloroethylene and the presence of those compounds in some dry-side spotting and pre-cleaning agents used in drycleaning contributes to the formation of hydrochloric acid and corrosion of metals in the drycleaning machine. Both 1,1,1-trichloroethane and trichloroethylene degrade at lower temperatures than PCE.

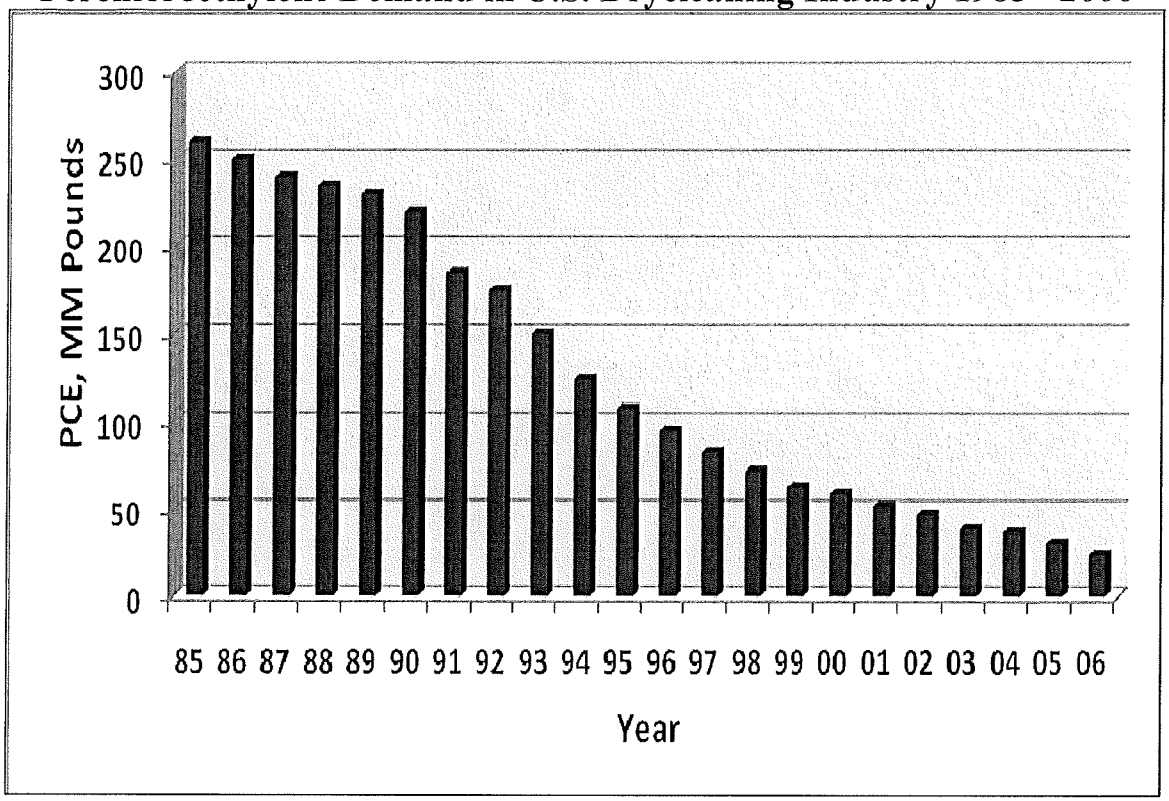
To combat this problem, drycleaning solvent manufacturers add stabilizers to PCE. These stabilizers function as antioxidants or oxidation inhibitors and acid acceptors, neutralizing the acidic PCE. Some of the early drycleaning-grade PCE stabilizers were benzotriazole related compounds (Knight, 1969). Other compounds that have been used to stabilize drycleaning-grade PCE are 4-methylmorpholine, diallylamine, tripropylene, cyclohexane oxide, betaethoxyproprionitrile, and 4-methoxyphenol. Concentrations of stabilizers in PCE range from 0.005% to 0.5% (by volume). In general, the concentrations of stabilizers in drycleaning grade PCE are lower than the concentrations of stabilizers in PCE and PCE/solvent blends using in degreasing operations. Other compounds that have been used as PCE stabilizers are 2,3-epoxypropyl isopropylether, 2,6-bis (1,1-dimethylethyl)-4-methylphenol, 2,4-di-tert-butylphenol, di-isopropylamine, tert-amylphenol and tert-butyl-glycidylether (European Community, 2005).

Some drycleaners purchase and use reclaimed PCE. This reclaimed solvent has a reported purity of 95 – 99%. Typical impurities in reclaimed PCE are: methyl ethyl ketone, mineral spirits, toluene, 1,1,1-trichloroethane and other chlorinated solvents. The spent PCE that is reclaimed does not come solely from drycleaning operations. Generally, stabilizers are not added to reclaimed PCE prior to it being sold. Reclaimed PCE is often blended by the drycleaner with commercial (stabilized) PCE prior to use in drycleaning. Drycleaning wholesale supply facilities sell PCE stabilizers. An example of such a product is Perchlor Type 236, marketed by PPG Industries, Inc. It is described as a perchloroethylene stabilizer concentrate and contains cyclohexane oxide, beta-ethoxy proprionitrile, n-methyl morpholine, and 4-methoxyphenol (PPG Industries, 1999).

PCE use in the United States peaked in 1980 and drycleaning was the largest user of PCE (Dougherty, 2000). Based on data collected in the 1980 Census, approximately 86.7% of U.S. drycleaners used PCE in 1980 (USDC, 1986). In 1990, the United States Environmental Protection Agency (U.S. E.P.A.) proposed national emission standards to limit PCE emissions from drycleaning plants. More drycleaners replaced transfer machines with dry-to-dry machines and improvements in the design of these machines resulted in reduced PCE emissions and higher solvent mileage, the amount of fabric cleaned per a quantity of solvent. As late as 1996, the drycleaning industry was still the largest user of PCE in the United States (Leder, 1999). In September of that year, E.P.A. issued National Emission Standard Hazardous Air Pollutants (NESHAP) Requirements which obligated PCE drycleaners to monitor emissions and keep records of drycleaning machine maintenance. In January of 2006, the California Air Resources Board voted to phase out PCE drycleaning by 2023 (California E.P.A., 2007). Under the Final Rule - National Perchloroethylene Air Emission Standards for Dry Cleaning Facilities, transfer machines could no longer be used in PCE drycleaning operations after July 27, 2008 (E.P.A., 2006). These actions have resulted in a

decline in the amount of PCE used by drycleaners and stimulated the introduction of alternative drycleaning solvents. According to the Halogenated Solvents Industry Alliance, by 2007, PCE was used by approximately 70% of U.S. commercial drycleaners and only 10% of the PCE used in the U.S. was for drycleaning/textile processing (HSIA, 2008).

Perchloroethylene Demand in U.S. Drycleaning Industry 1985 - 2006



Source: Textile Care Allied Trades Association

1,1,2-Trichlorotrifluoroethane

In 1964 E.I. DuPont de Nemours & Company introduced a chlorofluorocarbon drycleaning solvent known as 1,1,2-trichlorotrifluoroethane or Freon 113 (Johnson, 1971). Its trade name was Valclene®. Since the vapor pressure of Valclene® is approximately 20 times that of PCE, clothes cleaned in Valclene® could be dried at lower temperatures and it was therefore promoted as the solvent of choice for the drycleaning of delicate fabrics. Freon 113 is one of the chlorofluorocarbons subject to the Montreal Protocols and is no longer manufactured. It was never widely used in drycleaning and Valclene® drycleaning operations have either shut down or converted to other solvents.

1,1,1-Trichloroethane

In the early 1980s, Dow Chemical began marketing 1,1,1-trichloroethane (a.k.a. methyl chloroform or TCA) as a drycleaning solvent under the name Dowclene LS®. It was used particularly in leather cleaning operations. Reportedly, only approximately fifty (50) drycleaning plants in the United States ever used TCA as a primary solvent. TCA is not a very stable solvent and was heavily

stabilized. Despite this, there were problems with machine and equipment corrosion. TCA has been used as a pre-cleaning and spotting agent. It has also been used as a carrying agent in fabric waterproofing and in stain repellents.

Glycol Ethers

- **RYNEX® Biodegradable Dry Cleaning Solution:** Rynex® was the first glycol ether based drycleaning solvent. It was first marketed in 1999 (Hayday, 2007). It is a mixture or blend of aliphatic propylene glycol ethers. An earlier formulation of Rynex® reportedly contained propylene glycol t-butyl ether (PGtBE). The current product reportedly contains dipropylene glycol tert-butyl ether (DPTB) and is called Rynex® 3 (CARB, 2008). Rynex® has a flashpoint of >200° F and a specific gravity of 0.91.

- **Impress™** is described as aliphatic propylene glycol ethers. It has a flash point of 190.4° F and a relative density of ~ 0.922. It is manufactured by Lyondell Chemical Company and was first marketed in April of 2004 (Liotta, 2007).

- **GEN-X Drycleaning Fluid** is a blend of aliphatic Propylene Glycol Ether and hydrotreated heavy naphtha. It has a flashpoint of 160° F and a relative density of 0.830. It is marketed by Caled Industries.

- **Solvair™ Drycleaning System** is actually a drycleaning process that uses Solvair™ Fluid or dipropylene glycol n-butyl ether (dripropylene glycol normal butyl ether or DPnB) as a base cleaning fluid and then utilizes liquid carbon dioxide to rinse the garments. The system is marketed by R.R. Street.

Decamethylcylcopentasiloxane (GreenEarth™)

GreenEarth is a silicon-based solvent which was first marketed as a drycleaning solvent in 1999 (Maxwell, 2007). The chemical name for GreenEarth is decamethylcylcopentasiloxane, a.k.a D5. Its molecular formula is $C_{10}H_{30}O_5Si_5$. GreenEarth has a flash point of 170.6° F. and a specific gravity of 0.95.

n-Propyl Bromide

In October 2006 Drycleaning Technologies™, a division of Environ Tech International, Inc. began marketing Dry-Solv™, an n-propyl bromide (1-bromopropane) based drycleaning solvent (Roccon, 2007). The molecular formula for n-propyl bromide is C_3H_7Br. It has a specific gravity of 1.33. The MSDS for Dry-Solv™ indicates that the product is greater than 95% by weight n-propyl bromide. Dry-Solv™ is stabilized with nitromethane (<0.6%) and 1,2-butylene oxide (<0.6%).

In 2008, Tech Chem began marketing Tech Kleen for Dry Cleaning. Based on its MSDS, Tech Kleen for Drycleaning is >94% n-propyl bromide by weight and is stabilized with 1,2-epoxy butane (<1%).

PureDry™

PureDry™ was developed by Niran Technologies and was first marketed in 2000 (Eastern Research, 2005). It is described as a "hybrid" solvent and is a mixture containing 95% isoparaffinic hydrocarbons, (C_9 – C_{12} hydrocarbons), hydrofluoroethers (HFEs) and perfluoroisobutylethers (Eastern Research, 2005). PureDry™ has a flashpoint of 350 degrees F and a specific gravity of 0.80.

Liquid Carbon Dioxide

Liquid carbon dioxide is a cleaning process whereby carbon dioxide in a liquid state (operating under a pressure of between 700 to 800 pounds per square inch) is utilized as a solvent. The first commercial liquid carbon dioxide drycleaning plant opened in Wilmington, North Carolina in 1999 (Wentz, 2001).

OTHER CHEMICALS USED IN THE DRYCLEANING MACHINE

Detergents

Detergents are used in the drycleaning process. They perform three different functions:

- carry moisture to aid in the removal of water soluble soils;
- suspend soil after it has been removed from the fabric;
- and act as a spotting agent to penetrate the fabric so that the solvent and water can remove stains.

Based on their charge and how they carry water, there are three classifications of detergents:

- anionic detergents – are negatively charged and carry water by means of solubilization;
- non-anionic detergents - carry no charge and carry water by solubilization;
- cationic detergents – are positively charged and carry water by means of an emulsion. Most cationic detergents are pre-charged with moisture.

Detergents are introduced into the drycleaning machine by two different systems:

- In charged systems, detergent is added to the solvent or "charged" as a certain percentage of the solvent (normally 1 to 2%) to maintain a continuous concentration of detergent. Charged systems use anionic detergents. "Pre-charged solvent" (solvents containing the detergent) have been marketed in the industry, particularly for use in coin-operated drycleaning machines.

- In injection systems, also known as batched detergent injection, solvent is added to the wheel of the drycleaning saturating the garments and then detergent is injected into the flow line or into the drum of the drycleaning machine by a pump or dump method. Cationic detergents are used in injection systems.

The earliest drycleaning detergents were soaps. There were three different types: paste soaps, gel soaps and liquid soaps. Most of these soaps were composed of surfactants, Stoddard solvent, free

fatty acids and some moisture to create an emulsion. When filtration was first utilized in the drycleaning process to purify dirty solvent, it was discovered that paste and gel soaps, also known as "true soaps", tended to plug or "slime" the filters, so these soaps became obsolete. The liquid soaps, also known as "filter soaps", sometimes contained a co-solvent such as butyl cellosolve, hexylene glycol, isopropanol, cyclohexanol, ethanolamine or n-butanol, which was used to disperse moisture. By the early 1950s, the industry trend was from liquid soaps to the use of synthetic detergents.

Synthetic detergents are surfactants or mixtures of surfactants with solvents. The following surfactants have been used in commercial drycleaning detergents: soap-fatty acid mixtures; "mahogany" or petroleum sulfonates; sodium sulfosuccinates; sodium alkylarenesulfonates; amine alkylarenesulfonates; fatty acid esters of sorbitan, etc; ethoxylated alkanolamides; ethoxylated phenols; and ethoxylated phosphate esters (Kirk-Othmer, 1965).

The constituents listed for the drycleaning detergents in the drycleaning chemical data spreadsheet include surfactants: phosphate esters, linear alkylbenzenesulfonic acid salt, oxyethylated isononylphenol, diethanolamine, alkearyl sulfonate, sodium sufonate, and sulfosuccinate. They also include drycleaning solvents and co-solvents that function as carriers. These include perchloroethylene, petroleum solvents and the following cosolvents – butyl cellosolve, hexylene glycol, 2-propanol, isopropyl alcohol, 2-butoxyethanol, diethylene glycol monobutylether, dipropylene glycol monomethylether and glycol ether. The most common solvent contained in the drycleaning detergent mixtures listed on the spreadsheet is petroleum drycleaning solvent (petroleum naphtha blends).

Sizing

Sizing is a type of finish used in drycleaning to restore shape, body and texture to a fabric. Sizing is actually applied to fabrics when they are manufactured and is depleted after several fabric cleanings. Most sizing used in drycleaning operations today is composed of hydrocarbon resins (plastic-based). Alpha methylstyrene and styrene have been used in sizing in the past. There are two forms of sizing used in drycleaning operations, a solid (in a powder or bead form), and a liquid. The solid form of sizing - the bead form - is commonly used in PCE drycleaning systems. Most of the liquid sizing used today has a petroleum solvent carrier. It is not uncommon for liquid sizing to contain over 50% petroleum solvent (petroleum naphtha blends) by volume. Anti static agents and optical brighteners are commonly added to sizing.

Sizing can be applied in three different ways: by a continuous bath in the drycleaning machine; by dipping garments in a tank of sizing; or by spraying sizing in an aerosol form (generally containing a propane/isobutane carrier) on the garments after they have been drycleaned.

In the continuous bath application method a 0.5 to 1.5% charge of sizing is added to the drycleaning machine. The concentration of sizing used in the dipping application method ranges from 1 to 4% (Eisenhauer).

Other Chemicals

Other chemicals used in the drycleaning machine include: optical brighteners, bactericides, fabric conditioners, and anti-static/anti-lint agents

Optical brighteners, also known as fluorescent whitening agents, optical bleaches or optical dyes are used to "make whites whiter". These chemicals absorb the ultraviolet and violet region of colors in a fabric. These chemicals are normally added to drycleaning detergents or sizing. Optical brighteners have been widely used in laundry detergents for many years. In recent years, they have been used in drycleaning.

Some fabric conditioners are added to the drycleaning process. These are used primarily to condition or restore luster and shine to suede, leathers and silks. These products are typically solvent based – petroleum naphtha or perchloroethylene.

Anti-static agents and anti-lint agents (to prevent lint buildup and retention) are available for drycleaning operations. Some chemicals used in anti-static agents are sulfonated polystyrene or sulfonated polystyrene/maleic anhydride polymers.

PRE-CLEANING/SPOTTING AGENTS

The greatest number and variety of chemicals used in drycleaning operations are used in pre-cleaning and spot cleaning or operations. Prior to being placed in the drycleaning machine, heavily stained garments are usually pre-cleaned or pre-spotted with cleaning chemicals. The types of chemicals used depend on the type of stain and the type of fabric being cleaned. After they are drycleaned, garments that are still stained or soiled are spot cleaned using the same chemicals as in pre-cleaning. There are three types of pre-cleaning/spotting agents: wet-side agents, dry-side agents and bleaches.

Wet-side Spotting Agents

Wet-side pre-cleaning/spotting agents are used to clean water soluble stains from clothing. Wet-side agents can be subdivided into three different classes: neutral, alkaline, and acidic.

Neutral Wet-Side Agents – Neutral spotting agents include water and neutral synthetic detergents (which contain surfactants). These agents are used to remove water-soluble stains, food, beverages and water-soluble dyes.

Alkaline Wet-Side Agents – Alkaline spotting agents include lye, ammonia, potassium hydroxide, sodium hydroxide and so-called protein formula home detergents. Protein formula detergents contain digester enzymes - Amylase, Cellulase, Lipase and Protease. Digesters can be used to remove: starch, cellulose, fats and oils, and protein stains.

Acidic Wet-Side Agents – Acid agents include acetic acid, hydrofluoric acid, oxalic acid, glycolic acid and sulfuric acid. Tannin or plant-based stains can be removed with wet-side spotting agents also known as tannin formula agents.

Dry-Side Spotting Agents

Dry-side pre-cleaning/spotting agents are used to remove oily-type stains, stains including fats, waxes, grease, cosmetics, paints and plastics. The primary constituents of dry-side agents are non-aqueous solvents and alcohols and include, or have included: perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride, methylene chloride, amyl acetate, acetone, ethanol, methanol, isopropyl alcohol and petroleum solvents. In general, from a contamination and regulatory standpoint, dry-side spotting agents include some of the most toxic chemicals used in drycleaning operations.

Bleaches

Bleaches are used in stain removal when other spotting techniques have failed to remove a stain. This process is known as "spot bleaching". Bleaches are also used in conventional laundry operations which are conducted at most drycleaning plants. Bleaches can be classified as either oxidizing or reducing.

Oxidizing Bleaches	Reducing Bleaches
Sodium Perborate	Sodium Bisulfite
Hydrogen Peroxide	Sodium Hydrosulfite
Sodium Percarbonate	Titanium Sulfate
Sodium Hypochlorite	Oxalic Acid

GARMENT TREATMENT CHEMICALS

A number of different chemicals are used to treat garments after they are drycleaned. The functions of these chemicals include waterproofing, flame retardants, refurbishing, deodorizing, stain repellents and pest control.

Waterproofing

Waterproofing of garments by the clothing manufacturer is a relatively recent development. Historically, much of garment waterproofing was performed by drycleaners. In the past, the water proofing agent was usually a wax-based product and the predominant carrying agent for waterproofing agents has been nonaqueous solvents – perchloroethylene and petroleum solvents. Several methods have been used to apply the waterproofing agent, including immersion in the waterproofing agent in a dip tank; spraying the waterproofing agent on the garments in a tank; applying the waterproofing agent in the form of an aerosol spray; and in some cases applying the waterproofing agent in an auxiliary tank in a drycleaning machine (Rising, 1997).

Flame Retardants

Flame retardants are normally applied to garments by garment or textile manufacturers. Flame retardants can be depleted through repeated conventional laundering and drycleaning of garments. In the past, some drycleaners have treated or re-treated garments with flame retardants. Some of the chemicals used in flame retardants include: decabromodiphenyl oxide (DBDPO), organo-phosphates, phosphate salts and phosphated esters. Dry-side application of flame retardants used drycleaning solvent as the carrying agent. The flame retardant chemicals were applied by immersion or dipping in a tank or by spraying the garment with the flame retardant (IFI, 1995).

Fabric Conditioner

Chemicals are applied to refurbish garments after drycleaning. Typically, these garments can include suedes, leathers, silks, wools and vinyls. These chemicals are usually applied by spraying the garment (using a spray bottle or aerosol spray). Plasticizers such as di-N-butyl phthalate and di-2-ethylhexyl adipate are used to re-condition vinyl garments.

Stain Repellents

Stain repellents are generally applied by the garment manufacturer, but some drycleaners do apply stain repellents. Historically, these products have been silicone based and the carrying agent has been 1,1,1-trichloroethane (no longer used) or petroleum naphtha (IFI, 1994). Stain and water repellent chemicals used in drycleaning today use non-aqueous solvents as carrying agents (PCE, TCE, methylene chloride and petroleum solvents). A common constituent of many of these repellents is aluminum alcoholates. Most stain repellents can be applied as an aerosol spray.

CHEMICALS USED IN SOLVENT & EQUIPMENT MAINTENANCE

Solvent Maintenance & Treatment

From the early part of the twentieth century until the early 1950s, both alkalis and sulfuric acid were used to clarify spent petroleum drycleaning solvent. The most common alkali used was caustic soda (sodium hydroxide) in an 8-10% solution. The solvent was bubbled through or agitated with the caustic soda solution to help remove soap-fatty acid type detergents. Sulfuric acid was mixed and agitated with the spent solvent and the solids were then allowed to settle out (Martin, 1958).

Distillation of PCE solvent at high temperatures (> 300° F.) can result in the formation of hydrochloric acid in the distillation unit. Several chemicals have been used to neutralize acidic solvent/still bottoms in the distillation unit. These chemicals include sodium carbonate (soda ash), calcium carbonate and Alkanon, an alkali-aluminum silicate. The neutralization process consists of introducing an aqueous solution of the buffering compound into the distillation unit distilling the solvent.

Anti-foaming agents (commonly fluorosilicates) are sometimes added to the distillation unit to prevent contaminants in the spent solvents (pigments, fatty acids, filter powder, detergents water repellents and retexturing agents) from causing excessive foaming during the distillation process.

Detergents are sometimes added to the system to clean the drum and button trap of the drycleaning machine.

Filter Maintenance

Trisodium Phosphate was once used to clean tubular (regenerative) filters – used in powder filtration systems. It is doubtful that any of these tubular filters are still being utilized in drycleaning operations.

Detergent Maintenance

In charged systems, where anionic detergents are used, it is important to maintain a constant detergent concentration. Test kits are utilized to titrate solvent/detergent mixtures to measure the amount of detergent in the system. Chemicals used in these test kits can include: 1,2-dichloroethane, methylene chloride, and chloroform.

Boiler Maintenance

The use of untreated water in a boiler can cause scale buildup and corrosion. Treating the boiler water with chemicals - known as boiler feed water treatment - will increase the life of the boiler and reduce maintenance costs. Scale is formed from calcium and magnesium salts that are carried in solution in the water used in the boiler. Treatment of the boiler water by raising the pH with the addition of alkaline salts – such as sodium or potassium hydroxide – will prohibit most of the calcium and magnesium salts from precipitating and causing scale buildup in the boiler. Sodium sulfite is a constituent of some boiler feed water treatments. This constituent acts as an oxygen scavenger. The presence of oxygen in boiler water will lead to corrosion of the boiler (Faig, 1990). A chelating agent, sodium hexametaphosphate is sometimes added to boiler water to inhibit hard water salts from precipitating to form scale. Hydrochloric acid is sometimes utilized in acid boils to remove scale form the boiler.

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REFERENCES

Albergo, Nick. 1997. Letter from Nick Albergo, H.S.A. Environmental, to William J. Linn, FDEP.

Allsbrooks, Chris. November 2000. Use of Bleaches in Stain Removal. Silver Spring: International Fabricare Institute Industry Focus No. 2.

Andrasik, Maria J., M. Scalco. November 1989. Bleaches. Silver Spring: International Fabricare Institute Special Reporter, Vol. 17, No.4.

California Air Resources Board (CARB). October 2005. California Dry Cleaning Industry Technical Assessment Report (Draft). Stationary Sources Division, Emissions Assessment Branch.

California Air Resources Board (CARB). March 2008. Dry Cleaning Alternative Solvents: Health and Environmental Impacts. Sacramento: California Air Resources Board Fact Sheet.

California Environmental Protection Agency. January 2007. News Release. Sacramento: California Air Resources Board.

Calleja, Jay. January 2000. Stain Removal Chemicals: From A (Amyl Acetate) to Z (Zuds).

Chemical Week, 1953. Tri, Per and Carbon Tet. 72, 56.

Chemical Engineering News. 1963. New Dry-Cleaning system Under Field Test. Chemical Engineering New. November, 41, 28.

Chevron Phillips Chemical Company LP. 2003. EcoSolv® Drycleaning Fluid MSDS. The Woodlands: Chevron Phillips Chemical Company LP.

Childers, Everett. February 2008. The Fine Art of Efficient Finishing. American Drycleaner.

Doherty, Richard E. 2000. A History of the Production and use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichlroethane in the United States: part 1 – Historical Background; Carbon Tetrachloride and Tetrachloroethylene. Environmental Forensics, Volume p. 69-81.

Dembovsky, Len. 1991. Preventing Drycleaning Machine Corrosion by Solvent Maintenance. Caringbah: The Australian National Drycleaner. October 1991, pp 6-8.

Eastern Research Group. 2005. Control and Alternative Technologies Memorandum. Morrisville: Memorandum, Eastern Research Group to U.S. E.P.A.

Enviro tech International, Inc. 2007. DrySolv Material Safety Data Sheet. Melrose Park: Enviro Tech International, Inc.

European Chemicals Bureau. 2005. European Union Risk Assessment Report. Tetrachloroethylene. Italy: European Communities.

Eisenhauer, Paul. 1985. Use of Sizing in Drycleaning. Silver Spring: International Fabricare Institute Bulletin Reprint – Practical Operating Tips No. 199.

Enviro Tech International, Inc. 2006. Dry-Solv™ Material Safety Data Sheet. Melrose Park: Enviro Tech International, Inc.

Faig, Ken. November, 1988. Boiler Feed Water Treatment. Silver Spring: International Fabricare Institute Bulletin Reprint – Technical Operating Information No. 605.

Faig, Ken. November, 1990. Maintaining Your Boiler. Silver Spring: International Fabricare Institute Bulletin Reprint – Special Reporter, Vol. 18, No. 4.

Hayday, William. 2007. E-mail from William Hayday, Rynex Holdings, Ltd. To William J. Linn, Florida Department of Environmental Protection.

HSIA. Perchloroethylene White Paper. 2008. Washington D.C.: Halogenated Solvents Industry Alliance, Inc.

International Fabricare Institute Education Department. Detergents. Silver Spring: International Fabricare Institute Bulletin Reprint, Technical Operating Information No. 603.

International Fabricare Institute Education Department. Dryside and Wetside Spotting and Prespotting. Silver Spring: International Fabricare Institute Bulletin Reprint – Technical Operating Information No. 625.

International Fabricare Institute. 1995. Flame Retardant Finishes. Silver Spring: International Fabricare Institute Bulletin – Technical Operating Information No. 658.

International Fabricare Institute. November 1994. Stain and Soil Repellents on Upholstery Fabrics: Do They Protect or Harm? Silver Spring: International Fabricare Institute Industry Focus, No. 6.

Jackson, Richard E. V. Dwarakanath. Fall 1999. Chlorinated Degreasing Solvents: Physical-Chemical Properties Affecting Aquifer Contamination and Remediation. Groundwater Monitoring Review. Dublin: National Groundwater Association, p. 102 – 109.

Johnson, Albert E. 1971. Drycleaning. Watford: Merrow.

Kamra, Mohammed. September, 1992. Water. Silver Spring: International Fabricare Institute Industry Focus, Vol. 16 No. 4.

Kirk-Othmer. 1965. Encyclopedia of Chemical Technology. New York: John Wiley & Sons Inc., Volume 7.

Knight, Don B. 1969. Perchloroethylene Corrosion. Presentation at International Fabricare Institute Technical Conference, November 1969.

Leder, A. 1999. C2 Chlorinated Solvents. Chemical Industries Newsletter. January 1999.

Leppin, Betty. March 1992. Corrosion in Drycleaning Machines. International Fabricare Institute. Silver Spring: Focus on Drycleaning, Volume 16, No. 1.

Liotta, Frank J. 2007, E-mail form Frank J. Liotta, Lyondell Chemical to William j. Linn, Florida Department of Environmental Protection.

Martin, Albert R., G. P. Fulton. 1958. Drycleaning Technology and Theory. New York: Textile Book Publishers, Inc.

Maxwell, Tim. 2007. E-mail form Tim Maxwell, GreenEarth Cleaning to William J. Linn, Florida Department of Environmental Protection.

Michelsen, Edna M. 1957. Remembering the Years 1907 – 1957. Silver Spring: National Institute of Drycleaning.

Mohr, Thomas K. G. 2001. Solvent Stabilizers White Paper (prepublication copy). San Jose: Underground Storage Tank Program – Water Supply Division, Santa Clara Water District.

Phillips, Lorraine. February 1992. What Is Pre-spotting? Silver Spring: International Fabricare Institute Bulletin Reprint – Technical Operating Information No. 637.

PPG Industries, Inc. 1999. Perchlor Type 236 Material Safety Data Sheet. Pittsburg: PPG Industries, Inc.

Rising, Jane, Schwartz, S. 1997. Water/Stain Repellents. Silver Spring: International Fabricare Institute Bulletin – Technical Operating Information No. 666.

Roccon, Ray. 2007. E-mail form Ray Roccon, National Sales Manager, Drycleaning Technologies to William J. Linn, Florida Department of Environmental Protection.

Rynex. 2001. Rynex Fact Sheet. Woodbury: Rynex Holdings, Ltd.

Schreiner, James. 2001. Petroleum Solvent – What Am I buying? Lyons: National Coalition of Petroleum/Hydrocarbon Dry Cleaners. April Newsletter.

Sciences International, Inc. 1995. Toxicological Profile for Stoddard Solvent. Washington D.C.: U.S. Department of Health and Human Services Public Health Service, Agency for Toxic Substances and Disease Registry.

Spotting Procedures. Concord Custom Cleaners.

Tech Chem. 2008. Tech Kleen for Dry Cleaning Material Safety Data Sheet. Hilton Head: Tech Chem.

United States Department of Commerce. 1986. County Business Patterns for the United States. Washington D.C.: Bureau of Census.

United States Environmental Protection Agency. August 1989. Locating and Estimating Air Emissions from Sources of Perchloroethylene and Trichloroethylene. Triangle Park: Office of Air Quality.

United States Environmental Protection Agency. July 27, 2006. National Perchloroethylene Air Emission Standards for Dry Cleaning Facilities: Final Rule Part II. Washington D.C.: U.S. E.P.A. Federal Register, 40 CFR Part 63.

United States Patent & Trademark Office. August, 2001. United States Patent 6,273,919 – William A. Hayday.

Van Den Berg, J.H. December 1984. Corrosion Problems with the Cleaning Machine. Delft: Institute for Cleaning Techniques.

Van Den Berg, J.H. October 1985. Neutralizing of Acid PERC. Delft: Institute for Cleaning Technologies.

Wentz, Manfred. Keith R. Beck & V. Monfalcone III. 2001. Colorfastness of fabrics Cleaned in Liquid Carbon Dioxide. Research Triangle Park: American Association of Textile Chemists and Colorists, Vol. 1, No. 5.

Western States Drycleaners and Launderers Association. National Clothesline's Spotters Complete Guide.