

**Spotting Chemicals: Alternatives to Perchloroethylene and Trichloroethylene in the
Textile Cleaning Industry**

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EXECUTIVE SUMMARY

Perchloroethylene (PERC) and trichloroethylene (TCE) are used in the textile cleaning industry as Paint, Oil and Grease (POG) spotting agents. Spotting agents are used before or after cleaning in equipment to remove spots on garments. PERC and TCE are carcinogens. They are classified as Hazardous Air Pollutants by EPA and Toxic Air Contaminants by the California Air Resources Board. Both chemicals are listed on California's Proposition 65 and are listed hazardous wastes under the Resource Conservation and Recovery Act.

This project was sponsored by Cal/EPA's Department of Toxic Substances Control and the U.S. Environmental Protection Agency. It was conducted by the Institute for Research and Technical Assistance (IRTA), a nonprofit organization. The purpose of the project was to identify, test, develop and demonstrate low-VOC, low toxicity alternates to PERC and TCE POG spotting agents.

IRTA tested safer alternative spotting agents with seven textile cleaning facilities that have adopted alternatives to PERC dry cleaning. The alternative spotting agents were used in facilities that have hydrocarbon, Green Earth, carbon dioxide and water-based cleaning processes. The alternatives were used by each facility for one to five weeks on the facility garments.

The alternative spotting agents that proved to be effective are shown in Table E-1. One of the spotting agents, Cold Plus, is a commercial spotting product introduced to the market in the last year or so. The other spotting agents are cleaners that IRTA has tested successfully for other purposes.

Table E-1
Alternative Spotting Agents That Performed Effectively

<u>Spotting Agent</u>	<u>Type of Material</u>
Cold Plus	Water-Based Cleaner
Mirachem NP 2520	Water-Based Cleaner
Soy Gold 2500	Methyl Ester and Surfactants
DPM	Glycol Ether
90% Soy Gold 2500/10% Acetone	Blend
90% Soy Gold 2500/10% DPM	Blend
90% DPM/10% Acetone	Blend

IRTA conducted a cost analysis to compare the cost of using TCE spotting agents with the cost of using the alternatives. The results indicated that the cost of using the alternatives is lower than the cost of using TCE.

Waste streams from the textile cleaning process containing PERC or TCE are classified as hazardous waste. One of the advantages of using the alternative spotting agents is that

these waste streams may not be classified as hazardous waste. Another advantage is that workers and consumers would not be exposed to PERC or TCE during spotting of or in the wearing of the garments. The Department of Health Services Hazard Evaluation System & Information Service assisted IRTA in evaluating the toxicity of the alternative spotting agents based on their Material Safety Data Sheets. The findings indicate that the alternatives are lower in toxicity than PERC or TCE spotting chemicals.

This project demonstrates that there are a variety of effective cleaners that could be used as alternatives to PERC and TCE spotting agents in the textile cleaning industry. These include water-based cleaners, soy based cleaners, glycol ethers, acetone and blends of these cleaners.

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I. INTRODUCTION AND BACKGROUND

According to the California Air Resources Board (CARB), there are about 5,000 textile cleaning facilities in California. About two-thirds of these facilities use perchloroethylene (PERC) for dry cleaning garments. Approximately one-third of the cleaners in California have converted from PERC to various alternatives. The vast majority of the cleaners have adopted hydrocarbon. However, other technologies, including Green Earth which is a silicone based solvent, Rynex which is a glycol ether, carbon dioxide and water-based technologies that rely on water and detergent are also being adopted for textile cleaning.

Regardless of the technology that cleaners employ, they all perform spotting as part of the garment cleaning process. Cleaners use spotting agents to remove spots prior to cleaning the garments in the machine or after the garments have been cleaned in the machine. Many of the spotting agents historically contained PERC and now contain trichloroethylene (TCE). Both PERC and TCE are carcinogens, they are classified as Hazardous Air Pollutants (HAPs) by EPA, they are classified as Toxic Air Contaminants (TACs) in California, they are listed on Proposition 65 as substances known to cause cancer to the state of California and they are listed hazardous wastes under the Resource Conservation and Recovery Act (RCRA).

The Institute for Research and Technical Assistance (IRTA) is a nonprofit organization established in 1989. IRTA works with companies and whole industries to identify, test, develop and demonstrate low-VOC, low toxicity solvent alternatives. Under U.S. EPA's Pollution Prevention Grants program, Cal/EPA's Department of Toxic Substances Control contracted with IRTA to identify, develop, test and demonstrate safer spotting agents for textile cleaning.

PREVIOUS RELATED WORK

Over the last three years, IRTA completed two projects related to the current spotting chemical investigation. The first project, sponsored by CARB and U.S. EPA, was a technology assessment of alternatives to PERC dry cleaning. Part of this project involved sampling certain of the waste and effluent streams for some of the alternative cleaning methods. In some of the streams, IRTA identified TCE and PERC. CARB is currently proposing a phaseout of PERC dry cleaning in 2023 so cleaners in the state will be converting to alternative technologies increasingly over the next 15 years.

The second project, sponsored by DTSC, involved examining the characteristics of the hydrocarbon technology, the most widely used PERC alternative, in more detail. IRTA sampled waste streams from the hydrocarbon process and, again, found PERC and TCE. Although the PERC may have entered the waste streams from various sources, the obvious source of the TCE was spotting chemicals.

Since PERC and TCE are listed hazardous wastes, if they are present in a waste stream, the stream is classified as hazardous waste. Some waste and effluent streams generated from the PERC cleaning alternatives would not be classified as hazardous waste if they did not contain these substances. In addition, it could be less costly to dispose of these wastes if they did not contain PERC or TCE. As cleaners convert away from PERC dry cleaning over the next several years, it is important to eliminate PERC and TCE in spotting chemicals as well.

PROJECT APPROACH

Virtually all cleaning facilities, regardless of the cleaning technology they have, use so-called Paint, Oil and Grease or POG spotting agents for spotting garments. These spotting agents contain various solvents but the most widely used POGs contain TCE and there are others that contain PERC.

The motivation for this project was to find effective alternative POG spotting agents that do not contain PERC or TCE. One of the aims of the project was to find alternatives that are low in VOC content and have low toxicity. There are alternative POG spotting agents that do not contain PERC but cleaners do not believe they work effectively. IRTA identified several existing POG spotting agents that do not contain PERC or TCE but, in many cases, it is not clear what chemicals they do contain. Many of the suppliers claim trade secrets on the Material Safety Data Sheets (MSDSs) and IRTA did not want to test spotting agents that have unidentified components.

Because cleaners do not accept existing products and because it is not clear what materials are in existing products, IRTA tested only one existing product, a water-based cleaner. IRTA tested several other products and developed blends of other products used in different industries for cleaning. IRTA tested these alternatives in screening tests and selected the best seven cleaners for more extensive testing in cleaning facilities. IRTA worked with seven cleaners to test the alternatives and the cleaners used a variety of PERC dry cleaning alternative processes. IRTA wanted to make sure the alternative spotting agents would be effective for all of the alternative technologies that cleaners will adopt over the next several years.

STRUCTURE OF DOCUMENT

Section II of the document presents information on the waste stream analysis conducted in the earlier two projects. It describes the spotting procedure in more detail and identifies the POG spotting agents used today. Section III summarizes the alternatives that were tested and the tests that were conducted. The health and environmental characteristics of the current spotting agents and the alternatives are described in Section IV of the document. The section presents information on the regulations, the VOC content and the toxicity of the spotting agents used today and the alternatives. Finally, Section V summarizes the results and conclusions of the analysis.

II. SPOTTING AGENT CHARACTERISTICS

This section presents information on the spotting agents found in the waste and effluent streams in the textile cleaning industry. It focuses on relevant aspects of the analysis of the waste and effluent streams from IRTA's earlier CARB/U.S. EPA and DTSC projects. It then discusses the procedures used in spotting. Finally, it presents information on some of the current POG spotting agents used by cleaners throughout the industry.

WASTE AND EFFLUENT GENERATION AND RESULTS

The major alternatives to PERC dry cleaning are:

- Hydrocarbon dry cleaning;
- Green Earth, a silicone based dry cleaning process;
- Rynex, a glycol ether based dry cleaning process;
- Carbon dioxide cleaning; and
- Various water-based cleaning methods include traditional wet cleaning which involves immersing garments in water and detergent, icy water cleaning which is conducted with low temperature water and detergent and Green Jet which involves spraying garments with a water mist and detergent.

The hydrocarbon, Green Earth and Rynex processes use filters to remove particulate contaminants in the dry cleaning process. The filters or filter residue is disposed of as waste. These processes also often use distillation to separate the oily contaminants from the solvent; this results in a still bottom that is disposed of as waste. Finally, there is water present in the systems from a variety of sources. The water and solvent are physically separated and the solvent is reused in the process. The water, which still contains some solvent, is a waste stream. Most cleaners use evaporation to dispose of this separator water.

In the carbon dioxide process, there is no separator water but a still bottom containing a high concentration of detergent is generated. In the water-based cleaning processes, the wash and rinse effluents are discharged to the sewer.

Waste and Effluent Analysis From CARB/U.S. EPA Project

In the earlier project, IRTA worked with the Los Angeles County Sanitation Districts (LACSD) to analyze the waste and effluent streams. IRTA collected samples from facilities using alternative technologies and LACSD analyzed the samples in their lab.

IRTA and LACSD analyzed the samples for various components including toxic volatile and semi-volatile organics. LACSD used EPA Test Methods 601/602 or 624 for the volatile organics and EPA Test Method 625 for semi-volatile organics. PERC and TCE are toxic volatile organics.

The analysis results for the still bottoms and separator water for the Green Earth, hydrocarbon and Rynex processes and for the still bottoms for the carbon dioxide process indicated that there were no toxic volatile and semi-volatile components found above detection levels. This does not mean PERC and TCE were not present, however, because the samples were very dirty. As a result, LACSD had to dilute them substantially to analyze them and this may have reduced the concentration of volatiles to below detection levels.

IRTA also sampled the wash and rinse effluents from four facilities using water-based cleaning technologies in two rounds of sampling. In the first round of sampling, the results indicated that PERC or TCE were found in the effluent at three of the facilities. The results are shown in Table 2-1.

**Table 2-1
Water-Based Cleaning Effluent Results--First Round Sampling**

Facility	Toxic Organics (micrograms per liter)			
	PERC		TCE	
	Wash	Rinse	Wash	Rinse
Wet Cleaner #1	5,300	1,100	<200	<40
Wet Cleaner #2	<40	<40	5,100	3,200
Wet Cleaner #3	<200	<40	<200	<40
Wet Cleaner #4	<1,000	140	<1,000	<40

Note: Different dilutions were required for each facility so detection limits were also different.

The values in Table 2-1 that have the “less than” (<) sign in front of them are below the detection level. The values are different for different cleaners because different dilution levels were required. Taking this into account, three of the wet cleaners had PERC or TCE in the effluent streams that were above detection levels. Wet Cleaner #1 had high concentrations of PERC in both the wash and rinse effluent. Wet Cleaner #2 had high concentrations of TCE in both the wash and rinse effluent. Wet Cleaner #4 had PERC in the rinse effluent.

IRTA investigated further to determine the origin of the PERC and TCE in the effluent streams. Wet Cleaner #1 and Wet Cleaner #4 both had a wet cleaning machine and a PERC dry cleaning machine. Wet Cleaner #2 and Wet Cleaner #3 had only wet cleaning machines. Wet Cleaner #4 was using spotting chemicals containing PERC and Wet Cleaner #2 was using spotting chemicals containing TCE.

Table 2-2 presents the results of the second round of sampling. Before the second round of sampling, Wet Cleaner #1 removed the PERC machine and the spotting and finishing supervisor was replaced. PERC and TCE were found in the wash effluent. The new spotter may have begun using a TCE based spotting chemical. Wet Cleaner #2 stopped using the TCE based spotting agent when IRTA reported the results. No TCE was found in the second round of sampling at this facility. Wet Cleaner #4 removed the PERC

machine before the second round of sampling. Even so, PERC was still found in the wash and rinse effluents and might be present in the spotting chemicals.

**Table 2-2
Water-Based Cleaning Effluent Results--Second Round Sampling**

Facility	Toxic Organics (micrograms per liter)			
	PERC		TCE	
	Wash	Rinse	Wash	Rinse
Wet Cleaner #1	480	<100	510	<100
Wet Cleaner #2	<20	<20	<20	<20
Wet Cleaner #3	<200	<200	<100	<100
Wet Cleaner #4	83	82	<20	<20

Note: Different dilutions were required for each facility so detection limits were also different

Waste Analysis for DTSC Project

This project focused in more detail on the hydrocarbon alternative process which is being adopted widely by cleaners. IRTA sampled the sludge/still bottom and the separator water at eight hydrocarbon facilities. The DTSC Hazardous Materials Laboratory (HML) analyzed the samples for the presence of VOCs. The method used by HML was EPA Method 8260B “volatile organic compounds by GC/MS.”

A number of VOCs were present in the waste streams. Table 2-3 presents the results of the analysis for PERC and TCE. The figures show that PERC and/or TCE were present in at least one waste stream analyzed at each facility. In some cases, the concentrations were very high.

**Table 2-3
PERC and TCE Found in Waste Stream Analysis at Hydrocarbon Cleaners**

Facility	Separator Water Concentration (micrograms per liter)		Sludge Concentration (milligrams per kilogram)	
	PERC	TCE	PERC	TCE
	#1	30,000	9,000	19
#2	230	2,400	1,900	400
#3	ND	ND	3	ND
#4	6	ND	30	ND
#5	71	ND	ND	ND
#6	ND	ND	130	ND
#7	17	2	2	ND
#8	16,000	ND	12	ND

Note: ND is non-detectable.

Summary of Analysis Results

The analysis results indicate that PERC and/or TCE are present in most waste and effluent streams in the textile cleaning industry. The PERC may come from a variety of sources. First, it can come in as a residue on garments that were previously dry cleaned using PERC. Second, cross contamination might occur in facilities with a PERC dry cleaning machine and another technology. Third, the PERC may be present in the spotting chemicals. The TCE comes from only one source, spotting chemicals. As discussed below, many POG spotting agents contain TCE and they are widely used.

SPOTTING PROCEDURES AND SPOTTING CHEMICALS

Cleaners use POG spotting agents to remove several types of contaminants before and sometimes after the garments have been cleaned in the machine. These spotting agents are suitable for removing:

- tar;
- ink;
- shoe polish;
- mascara;
- lipstick;
- oil-based paints;
- nail polish; and
- crayon.

A number of different solvents are used in POG spotting agents. These include glycol ethers, mineral spirits, methyl ethyl ketone, acetates and various alcohols. Cleaners often find these solvents to be ineffective and many spotters prefer spotting agents that contain PERC and/or TCE. As mentioned earlier, PERC was extensively used in spotting agents in the past. Because cleaners were aware that PERC was under increasing scrutiny in the dry cleaning industry, the spotting chemicals were reformulated with TCE. Although TCE is also toxic, the industry perceived it as being less toxic than PERC.

There are a handful of suppliers that provide POG spotting agents to the industry. These include R.R Street & Company, Laidlaw, Adco and Caled. These suppliers package the POG spotting agents in quantities ranging from one gallon containers to 55-gallon drums. Distributors purchase the spotting agents from the suppliers and sell them to cleaners. Distributors in California include United Fabricare, HNS, McGregor and MDL.

IRTA worked with cleaners and suppliers to estimate the amount of TCE and PERC containing spotting agents that are sold in California. About 42,000 gallons of the TCE based spotting agents are sold in California annually. The concentration of TCE in the spotting agents ranges from 10 percent to 100 percent. One of the most widely used spotting agents containing TCE is called Picrin (see below); it contains 100 percent TCE. Assuming that all of the spotting agents are TCE and not PERC, and assuming an average concentration of TCE of 95 percent for all products, about 40,000 gallons of TCE are used annually in spotting. The density of TCE is 12.11 pounds per gallon so this amounts to 242 tons of TCE per year. A much smaller amount of PERC based spotting agents are

used annually, according to the suppliers. IRTA estimates the amount of PERC spotting agents used annually in California at 150 gallons or about one ton per year.

Cleaners IRTA worked with to test the alternatives during this project described and illustrated the proper process for spotting with POG agents. The garment is put on the spotting board which is similar to an ironing board. The spotting agent is applied to the spot on the garment using a squeeze bottle. It is rubbed in with a brush or bone used for that purpose. The spot is flushed with water from the steam supply. It is then dried with compressed air. The garment is placed aside for the next load in the machine. In some cases, spotting is performed after the garments go through the machine when the cleaning process does not successfully remove the spot. The procedure is the same as that described above.

Specific TCE and PERC Spotting Agents

MSDSs for several spotting agents containing TCE and a few containing PERC are shown in Appendix A. The most widely used POG spotting agent is Picrin which is offered by R.R. Street & Company. A product sheet describing its use and an MSDS are shown in appendix A. The MSDS indicates that Picrin contains about 100 percent TCE.

An MSDS for a product called Volatile Dry Spotter (V.D.S.) offered by Laidlaw is shown in Appendix A. The MSDS indicates that the product contains approximately 98 percent TCE.

Another product, called Fast P-R, is offered by Caled. A product sheet and an MSDS for this product are shown in Appendix A. The MSDS indicates that the concentration of TCE in the product is approximately 95 percent.

Adco offers a product called PURO which apparently contains TCE. A product sheet and a description of the contents of the product from the State Coalition for Remediation of Drycleaners are shown in Appendix A. The contents sheet indicates that the concentration of TCE is less than 100 percent. Another product offered by Adco called Semi-Wet apparently contains 50 percent TCE. A product sheet and a content sheet description are shown in Appendix A.

A contents sheet from the State Coalition for Remediation of Drycleaners for an R.R. Street product called 2-1 Formula is shown in Appendix A. The contents sheet indicates that the product contains less than 50 percent TCE.

A contents sheet from the State Coalition for Remediation of Drycleaners for a product offered by Pariser Industries, Inc., is shown in Appendix A. According to the contents sheet, the product, called P.O.G., contains 21.8 percent PERC.

An MSDS for a product offered by Fabritec International, called 6748 VOL Volatile Spotter, is shown in Appendix A. According to the MSDS, the product contains between

30 and 60 percent of an unidentified halogenated hydrocarbon which is likely to be TCE or PERC.

A contents sheet from the State Coalition for Remediation of Drycleaners for a product offered by A.L. Wilson Chemical Co. called TarGo is shown in Appendix A. The product contains 10 percent TCE.

III. ALTERNATIVES TESTING

During this project, IRTA tested one alternative spotting agent that is used as a spotting agent commercially, some other cleaning agents used for cleaning in other industries and blends of the other cleaning agents developed by IRTA specifically for the testing. IRTA screen tested the alternative cleaners and then took them to cleaning facilities so they could be tested by spotters. This section describes the tests of the alternative cleaning agents in detail. It also presents a cost analysis and comparison of the current and alternative spotting agents.

SCREENING TESTS OF ALTERNATIVE SPOTTING AGENTS

The screening tests were conducted to determine what types of cleaning agents used in other industries might be suitable as alternatives to PERC and TCE based POG spotting chemicals. The approach that was used was to obtain garments from Goodwill and select garments for the screening tests that were made of a variety of different fabrics. Stains of the type that are removed during spotting with POG spotting agents were put on the garments. Baseline cleaners and a range of different cleaning agents were then tested to see if they could effectively remove the spots. IRTA relied on two experienced textile cleaners to conduct the spotting and to judge the comparative cleaning ability of the cleaners.

Garments and Contaminants Used in Screening Tests

Some of the garments used in the screening tests and the contaminants that were put on them were:

- white shirt that appears to be made of polyester with an Elite Security decal contaminated with blue screen printing ink;
- yellow men's pants made of nylon and polyester contaminated with motor oil;
- blue men's shirt made of 100 percent cotton contaminated with black latex paint;
- tan men's dockers made of 100 percent cotton contaminated with red nail polish;
- beige women's pants made of cotton and spandex contaminated with mascara;
- gold men's jacket made of acetate contaminated with a black Sharpie marker;
- beige men's shirt made of raw silk contaminated with lipstick;
- beige men's pajama pants made of acetate and rayon contaminated with rubber cement; and
- beige men's cargo pants made of 100 percent cotton contaminated with blue ballpoint pen ink.

Pictures of some of these garments with the stains from the contaminants are shown in Figures 3-1 through 3-7.



Figure 3-1. White Shirt with Blue Screen Printing Ink.



Figure 3-2. Yellow Pants with Motor Oil.



Figure 3-3. Blue Shirt with Black Latex Paint.



Figure 3-4. Tan Dockers with Red Nail Polish.



Figure 3-5. Beige Pants with Mascara.



Figure 3-6. Gold Jacket with Black Sharpie Marker.



Figure 3-7. Beige Shirt with Lipstick.

Two owners of cleaning facilities who are experienced spotters tested the alternative spotting agents on the Goodwill garments and on some of the garments in their cleaning facilities. One spotter at one of these facilities also assisted in the screening tests. The procedure that was used was to test the alternative cleaners on the spots and to use the proper spotting techniques (rinse with steam and blow out with air) described earlier. The baseline spotting agents were Picrin and Pyratex, two POG spotting agents commonly used today.

Cleaners Used in Screening Tests

IRTA selected several different cleaning agents for the screening tests. IRTA wanted to find alternative POG spotting agents that were low in VOC content and low in toxicity. IRTA also wanted to select cleaning materials that would not lead to the classification of the waste and effluent streams in textile cleaning as hazardous waste. Some of the cleaning agents tested during screening did not meet these requirements but IRTA tested them to see if they were effective enough cleaners to be used in smaller concentrations with other cleaners. The cleaning agents selected for screening tests were:

- Cold Plus;
- Mirachem NP 2520;
- PWF-10;
- Soy Gold 1000;
- Soy Gold 2500;
- C-29;
- Acetone;
- 90 percent Soy Gold 2500/10 percent acetone;
- 90 percent C-29/10 percent acetone;
- VM&P;
- DB; and
- 90 percent DB/10 percent acetone.

Cold Plus is the only commercial spotting agent that was tested; it is a water-based cleaner. Mirachem NP 2520 is a water-based cleaner developed for cleaning in the screen printing industry. PWF-10 is a water-based cleaner used to clean oil and grease in the auto repair industry. IRTA has tested Soy Gold 1000 and Soy Gold 2500 for cleaning ink in the screen and lithographic printing industries and they are used in other cleaning applications; they are based on methyl esters and they have low VOC content. C-29 is a mineral spirit based cleaner used for cleaning ink in the lithographic printing industry; like soy, it is low in VOC content. Acetone is used for cleaning in many applications and it is not classified as a VOC. If it is present in a cleaning agent at or above 10 percent, the spent cleaner would be classified as hazardous waste (see discussion in the next section). IRTA tested it to see if it cleaned effectively and could be used as an ingredient at 10 percent or less concentration in a spotting chemical. VM&P is a mineral spirits based cleaner that is classified as a VOC. Again, it was investigated as a possible ingredient in a spotting chemical. DB is a glycol ether that is considered to be a non-VOC in CARB's consumer product regulations (see discussion of regulations in next section).

Results of Screening Tests

The results of the screening tests showed that two of the three water-based cleaners performed relatively well in the screening tests and one did not. The Soy Gold 1000 is not water rinseable and it could not be rinsed with the steam; because it could leave a ring, IRTA did not test the chemical further. The C-29 and VM&P mineral spirits based cleaners did not perform well and IRTA did not use them further. Acetone at 100 percent was a reasonably effective cleaner but dissolved part of an acetate garment; it did not have a negative effect at 10 percent concentration. IRTA decided to test acetone, which is a good cleaner, at only a 10 percent concentration in the alternative spotting agents.

Based on these conclusions, the cleaning agents that were selected for further testing as a result of the screening tests are:

- Cold Plus;
- Mirachem NP 2520;
- Soy Gold 2500;

- DB;
- 90 percent Soy Gold 2500/10 percent DB;
- 90 percent Soy Gold 2500/10 percent acetone; and
- 90 percent DB/10 percent acetone.

MSDSs for these cleaners and the components of the cleaners are shown in Appendix B. Part way through the project, IRTA became aware that DB which is called diethylene glycol monobutyl ether, an ethylene glycol ether, has higher toxicity than the propylene glycol ethers. IRTA decided to substitute DPM, a propylene glycol ether called dipropylene glycol monomethyl ether, for DB. An MSDS for DPM is also shown in Appendix B.

FIELD TESTS OF ALTERNATIVE SPOTTING AGENTS

The field testing of the alternative spotting agents was conducted at seven facilities that have a total of nine cleaning machines. The facilities and the cleaning technologies for which the alternative spotting agents were tested are:

- Crown Cleaners--hydrocarbon machine;
- Porter Ranch Cleaners--hydrocarbon machine and wet cleaning machine;
- Flair Cleaners--hydrocarbon machine and wet cleaning machine;
- Larsen's Cleaners--Green Earth machine;
- Village Cleaners--Green Jet machine;
- Royal Cleaners--carbon dioxide machine; and
- Imperial Cleaners--icy water machine.

As discussed earlier, most cleaners that are converting away from PERC are adopting hydrocarbon so IRTA tested the alternative spotting agents at three facilities where hydrocarbon is being used. IRTA also tested the spotting agents at one facility using Green Earth and one facility using carbon dioxide. IRTA tested the alternative spotting agents at four facilities that have water-based cleaning technologies. These included two cleaners using the traditional wet cleaning technology, one cleaner that uses the Green Jet technology and one cleaner that uses the icy water technology.

Approach to Field Testing

At each of the facilities, IRTA first tested the alternative spotting agents on Goodwill garments and ran them through the machine. This was necessary to ensure that none of the alternative spotting agents would leave a ring after they were cleaned with each of the different technologies. IRTA selected alternative spotting agents originally with this in mind. All of the alternatives that were selected as a result of the screening tests were either water soluble or water rinseable. As discussed in Section II, if spotters use proper procedures, they will flush the spot with steam (water) after the spotting agent is applied and then dry it before cleaning it in the machine. Since all of the alternatives are water soluble or rinseable, IRTA expected they would not leave a ring if the spotting were performed properly. In all cases, with every technology, none of the alternative spotting

agents left a ring when spotting was performed properly. In some cases, when spotting was not performed properly, the spotting agents did leave a ring.

After IRTA tested the selected alternatives initially on the Goodwill garments at some of the facilities to ensure they would not leave spots, IRTA and the spotters tested them on the cleaner’s garments. Generally one or more of the spotting agents performed better than others. IRTA observed that there were strong personal preferences and the preferred alternatives varied widely from facility to facility. IRTA provided larger quantities of the alternatives the spotters preferred and the spotters tested them routinely in scaled-up testing for one to five weeks on their garments in place of the POG spotting agent that are currently used. IRTA staff visited the facilities at least once a week during the testing to get feedback on the performance of the alternative spotting agents.

Results of Field Testing

Most of the owners or spotters who tested the alternatives thought that at least one of them was as good as the current POG spotting agent. All of the alternatives had some limitations but most owners and spotters indicated that even the POG spotting agents they use currently have limitations. This is why cleaners often use more than one POG spotting agent.

Table 3-1 shows the preferred spotting agents for the different facilities. One of the facilities, Larsen’s, tested only one alternative in the scaled-up testing. Several of the facilities tested most of the alternatives for at least a week. The facilities that tested DB and DPM and blends containing the two chemicals generally thought DPM performed better than DB.

**Table 3-1
Spotting Agents That Were Used and Performed Well in Scaled-Up Testing**

<u>Facility</u>	<u>Acceptable Alternative POG Spotting Agents</u>
Crown	DB/acetone, soy/DB, Mirachem NP 2520
Porter Ranch	DB/acetone, soy/DB, soy/acetone, DB
Flair	DB/acetone, soy/DB, soy/acetone, DB, Mirachem NP 2520, soy/DPM
Larsen’s	Soy
Village	Cold Plus, soy
Royal	DPM, Cold Plus, soy
Imperial	Cold Plus, soy/acetone, DPM

COST OF CURRENT AND ALTERNATIVE SPOTTING AGENTS

IRTA performed a limited cost analysis of the current spotting agents and the alternative spotting agents that were tested during this project. The baseline POG spotting agent used for the analysis was TCE. IRTA collected price information from suppliers for the price paid by cleaners for the spotting agent. The price ranged from about \$42 to \$50 per

gallon if the cleaner purchased the product in gallon quantities. The price of the alternative spotting agents was compared with TCE at a mid range price of \$46 per gallon.

Cold Plus is the only alternative that was tested that is currently a commercial product sold to the textile cleaning industry as a spotting agent. One local distributor indicates that the price of the spotting agent purchased in one gallon quantities is \$36 per gallon.

Three of the other alternative spotting agents, Soy Gold 2500, Mirachem NP 2520 and DPM, are commercial products sold for other applications but not currently sold as spotting agents to the textile cleaning industry. IRTA estimated the prices of these materials if purchased in one gallon quantities as spotting agents based on discussions with the suppliers of these chemicals and a company that would like to distribute them.

The Soy Gold 2500 can be purchased from the supplier at a price of \$12.50 per gallon for drum quantities. Assuming the markup by the distributor would double the price charged to dry cleaners, the price of the Soy Gold 2500 for this industry would be \$25 per gallon. The Mirachem NP 2520 supplier price is \$10 per gallon for drum quantities. Again, assuming the price would double from a distributor markup, the price of the Mirachem NP 2520 to dry cleaners would be \$20 per gallon. IRTA did not further evaluate DB as an alternative spotting agent because it is more toxic than DPM. A supplier indicates that the price of DPM is \$12.56 per gallon if purchased in drum quantities. Again assuming the distributor markup would double the price, the price of DPM to the dry cleaner would be \$25 per gallon.

For the other blends containing Soy Gold 2500, acetone and DPM, IRTA assumed the supplier would have to blend the chemicals before selling them in drum quantities to the distributor. IRTA obtained prices for the blended materials from a supplier. The blend of 90 percent Soy Gold 2500/10 percent acetone is priced at \$12.57 per gallon based on purchases of drum quantities. Assuming the distributor markup would double the price, the cleaner would pay about \$25 per gallon for the blend. For the blend of 90 percent Soy Gold 2500/10 percent DPM, the supplier estimated a price of \$12.91 per gallon based on drum purchases. Again, assuming the distributor markup would double the price, a cleaner would pay \$26 per gallon. For the blend of 90 percent DPM/10 percent acetone, the supplier would charge \$11.76 per gallon based on drum purchases. The distributor markup would double the price to \$24 per gallon.

Table 3-2 shows the cost comparison for the TCE based spotting chemicals and the alternatives tested in this project. Note that the analysis includes DPM rather than DB because DPM is lower in toxicity.

Table 3-2
Price Estimates of Current and Alternative Spotting Agents
Based on One Gallon Quantities

Spotting Agent	Price Per Gallon
TCE	\$46
Cold Plus	\$36
Soy Gold 2500	\$25
Mirachem NP 2520	\$20
DPM	\$25
90% Soy Gold 2500/10% Acetone	\$25
90% Soy Gold 2500/10% DPM	\$26
90% DPM/10% Acetone	\$24

The values of Table 3-2 show that the cost of the TCE based spotting chemicals is higher than the cost of all of the alternative spotting chemicals. Even if the distributor markup was substantially higher for the alternatives, they would still be less costly than TCE.

IV. HEALTH AND ENVIRONMENTAL CHARACTERISTICS OF ALTERNATIVES

This section describes the regulations that affect the alternatives and the toxicity of the alternatives. The DHS HESIS assisted IRTA in evaluating the toxicity of the alternatives based on the information on the MSDSs.

AIR REGULATIONS THAT APPLY TO SPOTTING CHEMICALS

In California, four or five suppliers sell spotting agents in large quantities to distributors. The distributors, in some cases, repackage the spotting agents in smaller quantities and sell them to cleaners along with other supplies like filters, hangers and dry cleaning agents. The local air districts have regulatory authority over spotting chemicals since they regulate VOCs and toxic materials used in industrial facilities. Textile cleaning operations are considered industrial facilities. CARB may also have regulatory authority over spotting chemicals. CARB and local air districts do not currently have regulations that affect spotting chemicals.

CARB and local air districts could regulate the VOC content of spotting chemicals. TCE is classified as a VOC but PERC is not classified as a VOC. Other components of the formulations containing TCE and PERC are classified as VOCs. These agencies could also regulate the use of spotting agents containing TACs. Both TCE and PERC are listed TACs; a few of the other components in some of the formulations are also classified as TACs. The regulatory agencies might forbid the use of spotting agents that contain chlorinated solvents like TCE or PERC, for example.

The alternatives that were tested during this project were selected to have low toxicity and low VOC content. Cold Plus and Mirachem NP 2520 are water-based cleaners that likely have low VOC content. Soy Gold 2500 alone and combined with glycol ethers and acetone, also has low VOC content, at less than 25 grams per liter. Acetone, an ingredient of the soy/acetone and DPM/acetone formulation, has a VOC content of zero since it is exempt from VOC regulations. The glycol ethers, DB and DPM, have high VOC content. In CARB's consumer product regulations, however, both glycol ethers would be classified as Low Vapor Pressure (LVP) materials. For purposes of the consumer product regulation, LVPs are considered to be non-VOCs. Local air districts, however, would regulate the glycol ethers as having very high VOC content.

WASTE REGULATIONS THAT APPLY TO SPOTTING CHEMICALS

TCE and PERC are listed hazardous wastes under RCRA. Both chemicals are listed in RCRA under F001 and F002. F001 specifies TCE and PERC used "in degreasing." F002 specifies TCE and PERC when they are spent and "all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures." The

MSDSs discussed in the last section all contained TCE or PERC in concentrations of 10 percent or more. Thus the spent materials would make the waste streams hazardous waste.

This means that any waste stream from one of the alternative technologies that contains these materials from spotting chemicals is classified as hazardous waste simply because of the presence of TCE or PERC. This applies to sludge generated from spin-disk filters, still bottoms generated from distillation, separator water and the effluent from water-based technologies. Since spotting chemicals may be the origin of the PERC and TCE that appear in the waste streams, textile cleaning facilities should use alternatives that do not contain these materials.

Under RCRA, F003 specifies several other non-halogenated spent solvents including acetone, one of the ingredients used in the alternative spotting chemicals tested by IRTA. It includes “all spent solvent mixtures/blends containing, before use, only the above spent non-halogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above non-halogenated solvents, and, a total of 10 percent or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.” IRTA used blends of acetone containing 10 percent acetone. To avoid having the waste streams from use of the alternative cleaning technologies classified as hazardous waste, commercial spotting chemical blends should contain no more than nine percent acetone.

TOXICITY OF SPOTTING AGENTS

As mentioned above, HESIS evaluated the MSDSs of some of the alternative spotting agents that were tested during this project. Today PERC and TCE are the POG spotting agents most widely used by cleaners, even those using alternative technologies for textile cleaning. PERC and TCE are both carcinogens. Several years ago, because PERC, the major dry cleaning agent, received negative publicity because it is a carcinogen, the suppliers and distributors converted away from the chemical in POG spotting agents. Although some of the POG spotting agents still contain PERC, the industry largely adopted TCE as an alternative. This was a poor choice since TCE is also a carcinogen and, unlike PERC, is classified as a VOC. It is not clear why the industry believed that TCE was a better choice than PERC.

Toxicity of PERC and TCE

PERC is a probable human carcinogen and several studies conducted recently link PERC exposure to leukemia and esophageal, bladder, colorectal and breast cancers. PERC exposure also can harm the digestive and nervous systems, blood, liver and urinary tract. Animal data also indicate that PERC can cause cancer and developmental damage.

Some occupational studies have shown that TCE produces central nervous system effects, as well as membrane, skin and gastrointestinal irritation and decreased appetite. Hepatotoxicity (liver cancer) has been associated primarily with TCE inhalation. Renal

failure has also been reported in concert with hepatic damage. Cardiac dysrhythmias may be induced by heavy TCE use in susceptible persons.

Toxicity of Alternative Spotting Agents

The alternative POG spotting agents evaluated during this project included two water-based cleaners, Cold Plus and Mirachem NP 2520. They also included Soy Gold 2500, acetone, DB, DPM and blends of these three materials.

The MSDSs for the two water-based cleaners indicate the materials contain no hazardous ingredients. Generally, water-based cleaners contain an appreciable amount of water. The toxicity of these two cleaners appears to be low.

The MSDS for Soy Gold 2500 indicates the material contains no hazardous ingredients. The soy cleaner is a fatty acid ester with added surfactants that make it water rinseable. HESIS indicates that, although there were no toxicity data on fatty acid esters in Toxnet, Scorecard and other chemical databases, they are not volatile, do not pose an inhalation hazard and are of low toxicity compared to organic solvents. The European Union, in conjunction with the U.S., is sponsoring research on vegetable oils and their fatty acid esters as substitutes for organic solvents in industrial processes.

Consistent with general solvent toxicity, overexposure to acetone affects the nervous system and causes skin and respiratory irritation. In the case of acetone, however, the threshold for producing these health effects is higher (the Permissible Exposure Limit or PEL of the acetone is 750 ppm) than for most other organic solvents. Thus, acetone is lower in toxicity than many other organic solvents.

The HESIS review indicates that ethylene based glycol ethers, including DB, can damage red blood cells and cause anemia. The propylene glycol ethers, including DPM, do not cause this problem and they are less volatile than the ethylene glycol ethers. However, they can produce neurotoxic effects through skin absorption as well as inhalation. As described earlier, IRTA stopped testing DB and, instead, used DPM part way through the project because DPM is lower in toxicity than DB.

V. SUMMARY AND CONCLUSIONS

The textile cleaning industry is undergoing a substantial change. The industry is converting away from PERC dry cleaning to a variety of solvent, carbon dioxide and water-based alternative processes. Cleaners rely heavily on spotting agents to remove the spots from garments before or after they are cleaned in the machines. Some of these materials, called POG spotting agents, are used for removing paint, oil and grease stains from garments. The major POG spotting agent used by cleaners contains TCE; other less widely used POG spotting agents contain PERC. Even many cleaners that have already converted to alternatives to PERC dry cleaning still use the POG spotting agents based on TCE and PERC.

PERC and TCE are carcinogens. They are classified as HAPs by EPA and TACs in California. Both solvents are listed on Proposition 65 and wastes from processes where PERC and TCE have been used for cleaning are classified as hazardous wastes. IRTA estimates that about 40,000 gallons per year of TCE is used in spotting chemicals and 150 gallons per year of PERC are used for that purpose.

There is a need to find effective POG spotting agents that could replace PERC and TCE. Although some POG spotting agents that do not contain PERC and TCE are on the market, cleaners have indicated that most do not work well. During this project, IRTA identified one new commercial product, Cold Plus, and developed several other materials that could be tested as safer alternatives. IRTA performed screening tests of several different types of cleaners to identify those that would be most effective. The screening tests were conducted on typical POG stains that were put on Goodwill garments made of a range of different fabrics. The screening tests helped IRTA to decide on which cleaning agents would be most effective to test in textile cleaning facilities.

The scaled-up testing was conducted at seven textile cleaning facilities that used a variety of PERC dry cleaning alternative technologies. The alternative spotting agents were tested for hydrocarbon, Green Earth, carbon dioxide and three water-based technologies. At each of the facilities, the spotting agents were tested on Goodwill garments and put through the machine. This was necessary to determine whether the spotting agent would leave a ring. In the proper spotting process, after the spotting agent is applied, it is rinsed with steam and dried with compressed air. IRTA deliberately selected alternatives that were water soluble or water rinseable. The results of the field tests indicated that none of the alternative spotting agents left a ring if spotting was performed properly. The spotting agents were then tested on each facility's garments. Those the spotters preferred were left for testing for one to five weeks. IRTA visited the facilities regularly to obtain feedback on whether the spotting agents were effective.

The spotters at the seven test facilities had personal preferences but all of the alternatives that were tested were judged to be effective by at least one of the facilities. Two water-based cleaners were tested and one of these is already a commercial product. Two glycol ethers, DB and DPM, were tested and found to be effective. One soy based cleaner was

tested and it performed well according to the spotters at some facilities. Various blends of soy, acetone, and the glycol ethers were also tested and judged to be effective. Because DB is a more toxic glycol ether than DPM, in the later testing, IRTA switched to this material. Table 5-1 shows the spotting agents that were successfully tested during the project.

**Table 5-1
Alternative Spotting Agents That Performed Effectively**

<u>Spotting Agent</u>	<u>Type of Material</u>
Cold Plus	Water-Based Cleaner
Mirachem NP 2520	Water-Based Cleaner
Soy Gold 2500	Methyl Ester and Surfactants
DPM	Glycol Ether
90% Soy Gold 2500/10% Acetone	Blend
90% Soy Gold 2500/10% DPM	Blend
90% DPM/10% Acetone	Blend

IRTA conducted a cost analysis which compared the cost of a TCE spotting agent with the cost of the alternative safer spotting agents. The results indicate that the cost of using the alternative spotting agents is lower than the cost of using TCE.

IRTA analyzed the regulations that affect spotting agents. When PERC and TCE from spotting agents are present in waste streams generated by textile cleaners, those streams are hazardous waste. Wastes from PERC dry cleaning alternative processes might not be considered to be hazardous wastes if PERC and TCE were not present. As a result, disposal of the wastes could be less costly. Both CARB and the local air districts in California may have jurisdiction over regulating the VOC and toxic content of spotting chemicals. The alternatives tested by IRTA were selected to have low VOC content and low toxicity.

HESIS assisted IRTA in evaluating the toxicity of the alternative spotting agents. The results of the analysis indicate that the alternative spotting agents tested during the project are lower in toxicity than PERC and TCE.

This project demonstrates that there are a variety of other safer materials that can be used in place of TCE and PERC spotting chemicals. These alternative materials were found to be effective for a variety of different textile cleaning processes. The alternatives are also less costly than TCE spotting chemicals used widely today.