

mortgage, sell, convey or otherwise dispose of real and personal property of every class and description in any of the states, districts, territories or colonies of the United States and in any and all foreign countries, subject to the laws of such state, district, territory, colony and country.

(j) In general, to carry on any other business in connection with the foregoing and to have and exercise all the powers conferred by the State of California upon corporations formed under the laws of the State of California.

(k) The foregoing clauses shall be construed both as objects and powers and it is hereby expressly provided that the foregoing enumeration of specific powers shall not be held to limit or restrict in any manner the powers of the corporation.

THIRD: The county in the State of California where the principal office for the transaction of the business of the corporation is located is the County of Los Angeles.

FOURTH: The number of directors of the corporation is three. The names and addresses of the persons who are appointed to act as the first directors are as follows:

<u>Name</u>	<u>Address</u>
H. P. Balderson	925 Domingo Drive San Gabriel, California
J. R. Singleton	8139 Dinsdale Street Downey, California
Tom K. Johns	10615 Haledon Street Downey, California

The number of directors may be changed from time to time by a bylaw fixing or changing the number duly adopted by the shareholders.

FIFTH: The total number of shares which the corporation is authorized to issue is One Million (1,000,000); all of said shares shall be of the same class; the par value of each share shall be One Dollar (\$1.00); and the aggregate par value of all shares shall be One Million Dollars (\$1,000,000).

SIXTH: All sales or transfers of shares shall be effectuated in the manner prescribed by and subject to the provisions and restrictions relative thereto contained in the bylaws of the corporation at the times of such respective sales or transfers.

SEVENTH: Subject to the right of shareholders to adopt, amend or repeal bylaws, bylaws, other than a bylaw or amendment thereof changing the authorized number of directors, may be adopted, amended or repealed by the Board of Directors.

EIGHTH: This corporation reserves the right to amend, alter, change or repeal any provisions contained in these Articles of Incorporation in the manner now or hereafter prescribed by statute, and all rights conferred upon shareholders herein are granted subject to this reservation.

IN WITNESS WHEREOF, we have hereunto set our

hands and seals this 7th day of February, 1964.

H. P. Balderson

H. P. Balderson

J. R. Singleton

J. R. Singleton

Tom K. Johns

Tom K. Johns

STATE OF CALIFORNIA)
) ss.
COUNTY OF LOS ANGELES)

On this 25th day of February, 1964, before me,
a notary public in and for said county and state, personally
appeared H. P. Balderson, J. R. Singleton, and Tom K. Johns,
known to me to be the persons whose names are subscribed to
and who executed the within instrument, and acknowledged
that they executed the same, and that they are the directors
named therein.

IN WITNESS WHEREOF, I have hereunto set my hand
and affixed my official seal the day and year above written.

Thomas E. Bunn, Jr.

Notary Public in and for said
County and State



My Commission Expires March 4 1964

THOMAS E. BUNN, JR.
WILEY D. BUNN
ATTORNEYS AT LAW
429 S. SPRING STREET
LOS ANGELES 12
MADISON 6-0269

Norris Sells Its Factory in Alhambra

Norris Thermador Corp. has sold its electronic plant in Alhambra to a group of former employees. W. E. Cranston, president, announced.

Cranston said the 17,000-sq.-ft. facility has been renamed Spatron, Inc. It will be headed by J. R. Singleton, a 27-year-old Norris employee who was formerly general manager of the plant.

The company has some 32 employees, Cranston said. The new company has purchased the production facilities on a five-year plant and has an option to purchase the building, he said.

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EXHIBIT 3.G-5

WHEN RECORDED MAIL TO:

79-1278681

RECEIVED
NOV 09 1979

JACOBS, WEISER, KANE, BALLMER &
BERKMAN, Agency Counsel
and OLIVER, STOEVER & LASKIN, Special Counsel

(SPACE BELOW FOR FILING STAMP ONLY)

LAW OFFICES
A PROFESSIONAL CORPORATION
1000 SANNEY BOULEVARD
LOS ANGELES, CALIFORNIA 90018
TELEPHONE: 624-9227

THE DOCUMENT TO WHICH THIS
STAMP IS APPLIED IS A
CERTIFICATE OF RECORDATION

Oct. 11, 1979
7557 330

Attorneys for Plaintiff

ATTEST NOV - 7 1979

John I. Cortez, County Clerk

BY HD DEPUTY

SUPERIOR COURT OF THE STATE OF CALIFORNIA
FOR THE COUNTY OF LOS ANGELES

FREE 9 0

ALHAMBRA REDEVELOPMENT AGENCY,)
Plaintiff,)
vs.)
NORRIS-THERMADOR CORPORATION,)
etc., et al.,)
Defendants.)

No. C 257 569
JUDGMENT AND FINAL ORDER
OF CONDEMNATION

RECORDED IN OFFICIAL RECORDS
OF LOS ANGELES COUNTY, CALIF.

27 Min. Past 3 P.M. NOV 13 1979

Registrar-Recorder

Pursuant to a written Stipulation heretofore filed in the
above entitled proceeding by and between the plaintiff Alhambra
Redevelopment Agency, by and between its attorneys Jacobs, Weiser,
Kane, Ballmer & Berkman, Agency Counsel, and Oliver, Stoever &
Laskin, Special Counsel, by William B. Barr, and defendant Norris
Industries, Inc., formerly known as Norris-Thermador Corporation,
by and through its attorneys R. James Shaffer and Ernest A. Canning,
by Ernest A. Canning; and defendant Spatron Incorporated, sued
and served herein as Spatron, Inc., by and through its attorney
Mark A. Smith, and defendant County of Los Angeles, by and through
its attorney John H. Larson, County Counsel, by Terry C. Smith,
Deputy County Counsel, that a Judgment and Final Order of

1 Condemnation may be made and entered herein in accordance with
2 the terms and conditions hereof, and without further notice to
3 said defendants; and it further appearing that defendant Southern
4 California Edison Company has filed a Disclaimer herein.

5 IT IS HEREBY FOUND AND DETERMINED:

6 That the use for which said real property is being acquired
7 is a use authorized by law and that the acquisition of said
8 property is necessary therefor.

9 There are no delinquent or current and special County real
10 property taxes due and owing to the defendant County of Los
11 Angeles as to the real property being condemned herein. By
12 execution of the Stipulation for Judgment and Final Order of
13 Condemnation herein, said defendant disclaims any interest in the
14 property being condemned, hereinafter described, and further
15 disclaims any interest in the condemnation award to be paid
16 herein.

17 That by execution of the Stipulation herein each of the
18 defendants waived the right to trial, Findings of Fact and
19 Conclusions of Law, Notice of Entry of Judgment in Condemnation
20 and Notice of Entry of Final Order of Condemnation.

21 That an Order for Prejudgment Possession was signed by Herbert
22 M. Klein, Judge Pro Tempore of the Superior Court on October 20,
23 1978, and became effective on January 25, 1979, authorizing plain-
24 tiff to take possession of said real property; and that plaintiff
25 deposited the sum of \$110,000.00 into Court as a security deposit.

26 That the fair market value of the real property as of the
27 date of valuation herein is the sum of \$132,290.

28 That the total compensation, award and damages to be paid

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A PROFESSIONAL CORPORATION
1000 SUNSET BOULEVARD
LOS ANGELES, CALIFORNIA 90016
TELEPHONE: 554-8357

1 herein is the sum of \$132,290.00, plus costs of suit.

2 Pursuant to CCP Section 1255.010, plaintiff has heretofore
3 deposited the sum of \$110,000.00. Upon application of the defen-
4 dant Norris Industries, Inc., the entire sum of \$110,000.00 has
5 been withdrawn from Court and paid to said defendant. Said pay-
6 ment constitutes the total just compensation to which said defen-
7 dant is entitled and no further payment to said defendant is to
8 be made through this judgment.

9 The defendant Spatron Incorporated is the owner of certain
10 items of fixtures and equipment which are deemed part of the
11 realty and which are compensable in this action. The fair market
12 value of the following items of fixtures and equipment is the
13 total sum of \$22,290.00.

14 7 - Desks, wood, double pedestal, 60 x 34", assorted

15 6 - 7 drawer; 1 - secretarial.

16 5 - Chairs

17 2 - posture, steel frame; 3 - swivel arm, wood, assorted.

18 1 - Card Index File, steel, Remington Rand, "Kardex" - 5 x 8
19 card size, 6 drawer

21 5 - Storage Units

22 2 - closed, painted wood; 3 - Lamination Racks, 85 x 42 x
23 51" hi, fabricated w/ 40 - metal slide-out tray capacity.

24 1 - Work Bench, 12 x 2', painted steel top on painted wood legs.

25 1 - Assembly Bench, steel,

26 20 x 4', conveyor type w/ 4 - Oval Steel Assembly plates;

27 1 - Arbor Press, size O, Dake; 3 - Inspection Lights; 3 - du-
28 plex outlets.

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OLIVER, UDOEYER & LARSON
A CORPORATION
1000 SUMMIT STREET
LOS ANGELES, CALIFORNIA 90012
TELEPHONE: 614-9947

LAW OFFICES
OLIVER, STOVER & LARSON
400 W. 10th Street
LOS ANGELES, CALIFORNIA 90015
TELEPHONE: 626-9857

- 1 1 - Pay-off Cradle, 8 reel capacity, fabricated.
- 2 1 - Soldering Machine, 4KVA, induction type, Model SI-42,
- 3 Sherman Industrial Electronics, s/n 5472-6.
- 4 1 - Bake Oven, walk-in Style RS-HD-4, Despatch, s/n 40681,
- 5 440V, on-slab, w/ controls, exhaustor-blower & through roof ducting.
- 6 18 LF - Monorail Craneway, on pipe column, w/ Air Hoist,
- 7 chain type, Keller.
- 8 1 - Concrete Lined Pit, +4' deep.
- 9 1 - Storage Unit of old Safe, 48 x 60" hi.
- 10 1 - Punch Press frame, O.B.I., 4 ton, Benchmaster w/ motor.
- 11 1 - Table.
- 12 2 - Pneumatic Presses.
- 13 1 - Table.
- 14 1 - Humidity Chamber, s/s exterior, 20 x 20 x 36" inside di-
- 15 mensions w/ 2 Taylor Recorders (5 readings) Cooling Fan, Circulat-
- 16 ing water, Heating Controls.
- 17 1 - Testing Oven (for under load and heat) w/ Recorder (time
- 18 & temperature).
- 19 1 - Deep Freeze Chamber, chest type, Tenney Engineering Inc.
- 20 1 - Concrete Foundation Block, 3 x 5 x 2' hi.
- 21 2 - Vacuum Table Voltmeters, Model 400D, Hewlet Packard.
- 22 1 - AC-DC Voltmeter, precision Type, Model AC-100A, Cali-
- 23 bration Standards Corp.
- 24 1 - Surge Current Tester.
- 25 1 - Oscilloscope, Heathkit.
- 26 1 - Test Unit of 3 Panelmeters: 2 - Voltmeters, Simpson;
- 27 1 - AC 0-300; 1 - DC 0-25; 1 DC Ammeter, Simpson; 0-25A.
- 28 /

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-4-

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ATTORNEYS AT LAW
1000 SUMMIT BUILDING
LOS ANGELES, CALIFORNIA 90018
TELEPHONE: 884-9287

- 1 1 - Industrial Analyzer, Model 639, Weston Electrical Instru-
- 2 ment Corp., s/n 3925.
- 3 1 - Inductance Standard, General Radio, 3 scales; 1 Henry;
- 4 10 Millihenry; 100 Millihenry.
- 5 1 - Impedance Bridge, Type 650-A, General Radio, s/n 1102.
- 6 1 - Potential Transformer, Model 311, Weston, s/n 2819.
- 7 1 - Variable Autotransformer, 30, Type 116-3-Powerstat,
- 8 Superior Electric, 0-100V.
- 9 1 - Standard Ratio Transformer, Model PT-4, Gertsch, s/n 125.
- 10 1 - Inductance Bridge, D & B in-house.
- 11 1 - Oscillator, Model M-2 RC, Southwestern Industrial Electronics
- 12 Co., s/n R525.
- 13 1 - Ratio Transformer, Model RT-60, Gertsch, s/n 307.
- 14 1 - Ratio Transformer, Model TRT-1, Gertsch, s/n 106.
- 15 1 - Portable Potentiometer, Model 126W3, Brown.
- 16 1 - Variable Autotransformer, 30, Type 236-3-Powerstat,
- 17 Superior, 0-440V.
- 18 2 - Baking Ovens (household type), Thermador, in one painted
- 19 wood cabinet w/ closed understorage.
- 20 1 - AC Voltmeter, Model 155, Weston, s/n 70801.
- 21 1 - DC Voltmeter, Model 80A-3-Volt Box, John Fluke Mfg. Co.,
- 22 s/n 146.
- 23 1 - Impedance Bridge, Model 650A, General Radio, s/n 2633.
- 24 1 - Electronic Shorted Turn Indicator, Model 101D, Kartron,
- 25 s/n 1340.
- 26 2 - Test Sets, Type S - 5300, Leeds & Northrup.
- 27 1 - Test Set w/ 2 - DC Milliammeters, Simpson.
- 28 1 - Tube Tester, Model 539B, Hickock.

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- 1 1 - Panel w/ 5 AC Voltmeters, Weston; 4 - Model 301, 0-10,
- 2 0-50, 0-150 & 0-300; 1 - Model 476, 0-15.
- 3 1 - Panel w/ 5 AC Voltmeters, Rectifier Type, Model 49, Simp-
- 4 son, 0-1, 0-10, 0-50, 0-150 & 0-1000.
- 6 1 - Panel w/ 12 Panelmeters; 9 - AC Voltmeters, assorted;
- 6 1 - DC Voltmeter, 0-15, Model 321, Triplat; 1 - Kilovoltmeter,
- 7 Model 476, Weston; 1 - AC Ammeter, 0-1, Model 476, Weston.
- 8 1 - Variable Air Condenser, Type-246PX, W.W. Lindsay, Jr.,
- 9 s/n 25.
- 10 1 - Portable Electric Pyrometer, 0-3000°F, Brown Instrument Co.,
- 11 s/n 44051.
- 12 2 - Wave Filters, High Pass Type 830F, General Radio, 1000 cps,
- 13 500 ohms.
- 14 1 - Pyrometer, 0-250F/0-1200C, Wheelco Instrument Co., s/n
- 15 45B0401.
- 16 1 - DC Voltmeter, 0-300V/0-750V, Jewell.
- 17 1 - AC-DC Volt/Ohmmeter; Model 410B, Hewlett Packard.
- 18 1 - AC-DC Milliammeter, Model 622, Weston, s/n 18771.
- 19 1 - Standard Inductance, 1 henry, Type 106M, General Radio,
- 20 s/n 2220.
- 21 1 - Standard Inductor, Type 1482-D, General Radio, s/n 4891.
- 22 1 - Standard Reactor, 40W, 236V, Sylvania.
- 23 1 - Toolroom Lathe, no I.D., w/ chuck.
- 24 1 - Drill Press, Buffalo, 7 1/2" throat - Floor Model.
- 25 1 - Immersion Test of double sink w/ heater, in painted wood
- 26 cabinet.
- 27 1 - Radial Arm Saw, 14", Comet, built into 12 1/2' wood work
- 28 table.

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 A CORPORATION
 1000 WILSON BOULEVARD
 LOS ANGELES, CALIFORNIA 90018
 TELEPHONE: 884-1887

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- 1 1 - Double End Tool Grinder w/ buffing wheel.
- 2 1 - Storage Unit, 96 x 26 x 48" hi, painted wood, w/ open
- 3 & closed understorage.
- 4 2 - Work Benches
- 5 1 - w/3 closed storage compartments; 1 - w/2 closed storage
- 6 compartments.
- 7 1 - Desk, wood AS IS.
- 8 2 - Open Storage Sections, painted wood
- 9 1 - 72 x 16 x 72" hi; 1 - 96 x 16 x 72" hi.
- 10 1 - Swivel Arm Chair, wood.
- 11 1 - Foreman's Desk.
- 12 1 - Tapesooter, 4".
- 13 1 - Low Lift Platform.
- 14 1 - Lot of Shelving, assorted.
- 15 1 - Open Shelving Section
- 16 1 - Card Index File, steel, 12 drawer "Kardex", 5 x 8" card size.
- 17 1 - Lot of Assorted Equipment including:
- 18 2 - Drafting Tables; 2 - Card Index Files; 1 - Drinking
- 19 Fountain; 2 - Side Chairs, reception type; 1 - Magazine/Coffee
- 20 Table; 2 - Swivel Arm Chairs
- 21 1 - Refrigerator, Coldspot.
- 22 The total compensation, award and damages to be paid to the
- 23 defendant Spatron. Incorporated herein is the sum of \$22,290.00.
- 24 Payment of such amount to said defendant or into Court for its
- 25 benefit shall constitute the total just compensation to which
- 26 said defendant is entitled in this proceeding.
- 27 IT IS HEREBY ORDERED, ADJUDGED AND DECREED that the sum of
- 28 \$22,290.00 is for the benefit of and shall be paid and distributed

LAW OFFICES
 OLIVER, STOEVE & LASKIN
 A PROFESSIONAL CORPORATION
 1000 STREET BROADWAY
 LOS ANGELES, CALIFORNIA 90012
 TELEPHONE: 818-982-8877

1 as follows:

2 TO: Spatron, Incorporated, c/o Mark A. Smith, Esq.,
3 24551 Raymond Way, Suite 150, Lake Forest-El Toro,
4 California 92630, the sum of \$22,290.00.

5 IT IS HEREBY FURTHER ORDERED, ADJUDGED AND DECREED that
6 payment into Court for the benefit of the defendants of the sums
7 hereinabove specified shall constitute payment in full for
8 the real property taken and for all damages of any kind and
9 nature whatsoever suffered by the defendants by reason of such
10 taking.

11 IT IS HEREBY FURTHER ORDERED, ADJUDGED AND DECREED that the
12 following described real property is hereby condemned in fee simple
13 for the public use and purposes described in the Complaint herein,
14 to wit, the elimination of blight and for redevelopment purposes,
15 plaintiff to take title to said real property, together with
16 all improvements thereon, free and clear of any and all liens,
17 encumbrances, easements, leaseholds, current and delinquent
18 taxes and assessments, of whatever kind or nature.

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LAW OFFICE
OLIVER, STORVER & LASHON
1000 BROADWAY, SUITE 1000
LOS ANGELES, CALIFORNIA 90018
TELEPHONE: 444-9317

7-11-79

9

1 (Commonly known as 715 South Raymond Avenue, Alhambra,
 2 California)
 3 Lots 13 and 14 in Block 5 of Subdivision No. 1 of Dolgeville,
 4 in the City of Alhambra, as per map recorded in Book 5, Page 16
 5 of Maps, in the Office of the County Recorder of the County of Los
 6 Angeles.

7 EXCEPTING AND RESERVING to the owners thereof all oil, gas
 8 and mineral substances, together with the right to explore for,
 9 and extract such substances, provided that the surface opening of
 10 any well, hole, shaft or other means of exploring for, reaching or
 11 extracting such substances shall not be located within the
 12 INDUSTRIAL REDEVELOPMENT PROJECT area as recorded in Book M 3437,
 13 Page 437 of Los Angeles County Records, State of California, and
 14 shall not penetrate any part of or portion of said Project area
 15 within 500 feet of the surface thereof.

16 The Clerk is ordered to enter this Judgment and Final Order
 17 of Condemnation.

18 Dated: OCT 11 1979

Herbert M. Klein
 JUDGE OF THE SUPERIOR COURT

79 1278681

LAW OFFICE
 OLIVER, STOVNER & LAMBIN
 A PROFESSIONAL CORPORATION
 1000 SUNSET BOULEVARD
 LOS ANGELES, CALIFORNIA 90012
 TELEPHONE: 854-9127

EXHIBIT 3.G-6

CALIFORNIA MANUFACTURERS

Annual

REGISTER

1965

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Spasors Electronics Corp 1090 Morcna Blvd
San Diego 92110 276-5530
S.I.C. 3811
Pres Irving Reynolds
V Pres-Gen Mgr C Ross Fisher
Sales Mgr S W Hedrick
Product—Electronic Altimeters, Altitude Rate Meas-
uring Systems, Audio Warning Devices
Employs—10

Spatron Inc 715 S Raymond Alhambra CU 3-8831
S.I.C. 3679
Pres J R Singleton
V Pres H P Balderson
Sec-Treas T K Johns
Chief Eng W A Liebermann
Product—Transformers, Chokes, Filters, Reactors;
Transistorized Power Supplies, Inverters and Con-
verters; Transistorized Voltage Sensing Devices;
Magnetic Amplifiers and Voltage Regulators
Employs—50

Spaulding Fibre Company Inc 2000 Hoefner Ave
City of Commerce OV 3-6710
S.I.C. 3079
Pres R F Oleksiak
V Pres Mktg E C Leitz
V Pres E R Waitt (New Hampshire Div)
V Pres-Sec T C Drees
V Pres-Treas A H Rohrbaugh
V Pres-Tech Dir G A Cypber
Mgr West Coast C W Kuhn
Product—Laminated Thermosetting Plastics - Phen-
olic, Melamine, Epoxy - Vulcanized Fibre - Ar-
mitte (Thin Insulation) SPAULDING Motor Insula-
tion - SPAULDING Fibreboard and Transformer
Board - Material Handling Equipment (Trucks,
Boxes, Barrels, Trays, Etc) Complete Fabrication
Facilities in Los Angeles for Fabrication of Lami-
nated Thermosetting Plastics, Vulcanized Fibre
and Material Handling Equipment, Film and
Wound Tubes & Structures (for Electronics)
Capital—A Employs—40
Main Office Tonawanda New York
No Calif Sales Office 727 Industrial Rd San Carlos
LY 3-8421

Spears-Wells Machinery Co 1832 9th St P O Box 4036
Oakland 23 451-3432
S.I.C. 3711
Pres Milton Wilson Jr
V Pres & Gen Mgr A J Friedrich
Sec Lenore See
Service Mgr C M Todd
Product—Road Oil Distributors, Highway Brooms,
Heater Planers, Sand and Gravel Spreaders, Water
Sprinklers
Capital—BC Employs—12

Speas Co 46 Walker St Watsonville PA 4-7249
S.I.C. 2099
Mgr G W Leikam
Product—Vinegar and Pectin
Employs—8

Speas Co Vinegar Manufacturers 444 Roosevelt Ave
Montebello PA 8-4303
S.I.C. 2099
Gen Mgr Ron McCoy
Product—Vinegar

Spebra Products Manufacturing Company Inc
2017 Granville Ave Los Angeles 25 GR 9-1495
S.I.C. 2820
Pres Dr George B Smigel
Product—Chemicals for the Food and Beverage In-
dustries; Protectit Tank Lining & Protectit Pro-
viding a Stainless Steel Tank Lining & Mainte-
nance Coating Applied Cold, Beerstone Remover,
Brewers' Pitch, Chillproofing Compound, Spebra-
sept Disinfectant
Brand Name—Spebrasept, Spebra and Protectit
Employs—8
Branch Plants Nassau Bahamas British West Indies,
London England, Paris France

SPECIAL CUTTING TOOLS INC
4178 E Washington Blvd Los Angeles 23 AN 2-1127
S.I.C. 3541
Pres & Gen Mgr James G Bliss
V Pres Michael N Haprov
Office Mgr Jackson Bliss
Sales Mgr Robert Priest
Products—Carbide and High Speed Cutting Tools,
Engineered, Designed and Manufactured
Brand Name—"Specto"
Capital—D Employs—20

Special Tools & Machinery Co 4626 Pacific Blvd
Los Angeles 58 LU 9-6171
S.I.C. 3544
Pres Don P Vokal
V Pres and Gen Mgr Dick Graves
V Pres Sales Ed Frock
Supt Fred Marlow
Purch Agt Les Cleland
Product—Designing and Building Special Equipment
Dies, Jigs, Designing of Automatic Machinery and
Special Machinery, Fixtures, Special Aircraft
Parts, Precision Machining, Metal Stampings, Pre-
cision Grinding, Certified Welding
Capital—AB Employs—90
Subsidiary Company Vokal Metal Stamping Corp
4626 Pacific Blvd Los Angeles 58

Specialized Plating 2240 Cleveland Ave National City
477-3332
S.I.C. 3471
Prop Mario Vismara
Product—Anodizing and Plating

SPECIALIZED PLATING CO 11100 Missouri Ave
Los Angeles 25 478-0191 272-7856
S.I.C. 3471
Owner Carl R Klinefelter
Product—Plating, Licensed Vacuum Cadmium
(VAC-CAD), Anodizing, Vacuum Metallizing,
Painting
Employs—20

Specialized Welders 1843 W Artesia Blvd Gardena
FA 1-1612 DA 9-4794
S.I.C. 3591
Owner Wm Gudish
Product—Heliarc Welding, Aluminum, Stainless
Steel, Certified Aircraft Welding
Capital—CD Employs—10

Specialty Engineers Co 6003 Market St Oakland 8
(See Alphabetical Listing for Phillips Associates)

Specialty Foundry & Mfg Co 8805 Avalon
Los Angeles 90003 PL 9-9241
S.I.C. 3362
Owner Frank A Book
Product—Castings of Brass, Bronze, Aluminum and
Non-Ferrous
Capital—BC Employs—3

Specialty Industries Inc 2324 Washington Blvd
Venice 90291 EX 6-5585
S.I.C. 2499
Pres P R Masson
V Pres J Voyde
Product—Wood Products, Water Skis & Novelties

Specialty Machine Works 568 N Ave 23
Los Angeles 90065 CA 1-0954
S.I.C. 3591
Prop Rolfe E Whitaker
Product—Machine Parts, AN Fittings

Specialty Paper Box Co (a Corp) 6310 Avalon Blvd
Los Angeles 3 232-8164
S.I.C. 2652
Pres Max R Ginsburg
V Pres Irwin Gebroe
Plant Mgr Wm Lane
Sales Mgr Harry Lewis
Product—Rigid Paper Boxes
Capital—B Employs—125

1979

32nd Edition

**CALIFORNIA
MANUFACTURERS
REGISTER**

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CALIFORNIA MANUFACTURERS ASSOCIATION

Publisher

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Spartan Mfg Co (Continued)

Garden Grove 92642
(714) 531-2600
SIC 3452 Estab. 1956 Sales C
Pres David D Speaks Sr
Mgr Roy E Jolliffe
Purch Agt Stanley Speaks
Product—screw machine products
Employs—25

Spartan Truck Equipment

12266 Branford St Sun Valley 91352
(714) 899-1111
SIC 3550 Estab. 1973 Sales C
Pres & Gen Mgr John Germann
Sec-Treas Joan Germann
Purch Agt & Pers Mgr Clark Shellon
Product—solid waste handling equipment; repair & modify solid waste handling equip
Employs—18

Spatial Data Systems Inc

(PO Box 249) 508 S Fairview Ave
Goleta 93017
(805) 967-2383
SIC 3573 Estab. 1966 Sales C
Pres & Gen Mgr David F Rutland
V Pres M S Schlosser
Purch Agt Julie Raffety
Chief Eng Richard Colvin
Product—color systems, displays, and image digitizer
Brand Names: Datalcolor, Graficolor, Eye Com
Employs—24 Export

Spatron Inc

715 S Raymond Alhambra 91803
(213) 283-8831
SIC 3679 Estab. 1964 Sales B
Pres J R Singleton
V Pres H P Balderson
Sec-Treas T K Johns
Prod Mgr W J Brown
Product—transformers, chokes, filters, reactors; transistorized power supplies, inverters and converters; transistorized voltage sensing devices; magnetic amplifiers and voltage regulators
Employs—50 Export

Spatz Laboratories

4131 Glencoe Ave Venice 90291
(213) 821-8068 L A Phone (213) 870-5993
SIC 3079 Estab. 1956 Sales D
Pres W Spatz
Gen Mgr Jerry Powers
Product—cosmetic containers, lipstick cases, brushes, dispensers, decorating, packaging, injection molding
Employs—350 Import/Export

Spaulding Fibre Company

See Monogram Industries Inc

Spaulding Instruments

275 N Halsead Pasadena 91107
(213) 351-8924
SIC 3622 Estab. 1965 Sales D
Pres Carl P Spaulding
V Pres Monte L Marks
Sales Mgr L D Cassidy
Product—digital readout for machine tools
Export

Speas Co

46 Walker St Watsonville 95076
(408) 728-2061
SIC 2099 Estab. 1888 Sales D
Mgr H R King
Product—vinegar and pectin
Employs—20 Import/Export
Home Office Kansas City Mo

Speas Co Vinegar Manufacturers

444 Roosevelt Ave Montebello 90540
(213) 728-0142
SIC 2099 Estab. 1888
Gen Mgr Ron McCoy

Product—vinegar
Employs—14

Special Cutting Tools Inc

9844 Alburis Ave Santa Fe Springs 90670
(213) 692-0323 L.A. (213) 685-5926
Orange Co (714) 521-7740
SIC 3541 Estab. 1958 Sales C
Pres & Gen Mgr James G Bliss
V Pres Ernest Prisbe
Sales Don Neffinger
Spec Prod Mgr Richard Bender
Product—carbide and high speed cutting tools, broaches, engineer design
Brand Name—Specto
Employs—35 Import/Export

Specialized Automotive Engineering Inc

11535 Bradley Ave San Fernando 91340
(213) 361-7188
SIC 3714 Sales D
Pres Charles A Barnow
Product—four wheel drive mini pickup truck conversion; power steering & disc brake systems, positraction differentials; specialized applications for automatic transmissions
Employs—14 Export
Branch Plant:
Conversions Unlimited
637 E Arques Ave Sunnyvale 94086

Specialized Processing

581 S Marshall Ave El Cajon 92020
(714) 442-0663
SIC 3471 Estab. 1955 Sales C
Prop Mario Vismara
Product—anodizing and plating, shot peening, vacuum plating
Employs—25

Specialized Welders

505 Van Ness Ave Torrance 90501
(213) 775-2207
SIC 3599 Estab. 1949 Sales C
Pres Wm Gudish
Product—sheet metals, plate and gauge fabrication and production
Employs—20 Export

Specialized Yachting Services Inc

1 N Amphlett Blvd San Mateo 94401
(415) 342-5625
SIC 2394 Estab. 1969 Sales A
Pres Robert D Botley
Product—covers, yacht curtains, curtain kits, cushions; sail maintenance
Employs—5

Special Products Industries

See Best Seam Incorporated

Special Tools & Machinery Co

4626 Pacific Blvd Los Angeles 90058
(213) 589-6171
SIC 3544 Estab. 1924 Sales D
Pres Don P Vokal
V Pres and Gen Mgr Dick Graves
V Pres Sales Ed Frock
V Pres Mgr Fred Marlow
Sec-Treas John J Mesko
Purch Agt Bob Boggess
Product—special equipment, jigs, fixtures, aircraft parts, machining, grinding, optical tooling; welding, numerical control milling, drilling, turning
Employs—90

Specialty Brands Inc

850 Montgomery St San Francisco 94133
(415) 397-7550
SIC 2099 Estab. 1969 Sales F
Pres Toby Schreiber
V Pres & Treas Richard P Hanes
V Pres Mgr Fred Caligiuri
V Pres Mktg Robert W Maier
V Pres & Gen Sales Mgr Robert Cameron
V Pres R&D Dr John C Walts
Procurement Mgr Neal Brunckhorst
Product—spices, herbs & seasonings, refrigerated salad dressings

Employs—160 Import/Export
Office: 345 Allerton Ave So San Francisco Ca 94080
Plant: Sparks Nevada
Farm: Rt 1 Box 250 Dixon Ca 95620

Specialty Breads Inc

(Bohemian Bakery)
1245 Market St San Diego 92101
(714) 234-2195
SIC 2051 Estab. 1904 Sales D
Pres F Fornaca
Gen Mgr Ralph Cooper
Product—bakery products
Employs—45

Specialty Coatings & Chemicals Inc

7360 Varna Ave North Hollywood 91605
(213) 983-0055 (213) 875-0055
SIC 2851 Estab. 1964 Sales D
Pres Henry C Jacoby
V Pres & Sec-Treas Robert Mischel
Product—coatings, adhesives, cements, chemical specialties
Employs—25 Export

Specialty Design Inc

Sub of Eide Industries Inc
640 S San Pedro St Los Angeles 90014
(213) 627-7331
SIC 2394 Estab. 1973 Sales B
Pres James A Stapenhill
V Pres Jack R Eide
V Pres George K Ochs
Sec-Treas Donald J Araiza
Product—parachutes, aerodynamic decelerators and recovery systems

Specialty Fasteners/A Rexford Company

See Tridair Industries

Specialty Finishes Co

Division of Specialty Coatings Co
(PO Box 691) 9123 Center Ave
Cucamonga 91730
(714) 987-4687
SIC 3952 Estab. 1966 Sales C
Gen Mgr Joe Tamura
Product—industrial coatings
Employs—8 Export

Specialty Foundry & Mfg Co

6130 Valley View Buena Park 90620
(714) 522-3432
SIC 3362 Estab. 1938 Sales A
Owner Frank A Book
Product—castings of brass, bronze, aluminum and non-ferrous
Employs—4

Specialty Molders Inc

18275 Mt Baldy Circle
Fountain Valley 92707
(714) 962-6648
SIC 3069 Estab. 1961 Sales B
Pres F Dudley Case
V Pres Eleanor D Case
Supt Greg Toberman
Product—molded rubber, car racks
Employs—15 Export

Specialty Motors Inc

12863 Foothill Blvd San Fernando 91342
(213) 365-0811
SIC 3621 Estab. 1972 Sales D
Pres Kenneth A Stone
Sec-Treas Lois R Stone
Gen Mgr Kenneth A Stone
Chief Eng Don Still
Production Mgr Ronald L Grassette
Product—fractional hp electric motors
Employs—35 Import/Export

Specialty Organics Inc

5263 N 4th St Irwindale 91706
(213) 962-2008
SIC 7391 Sales C
Pres Joseph Seruto

Sec-Treas M Seruto
Product—synthesis of commurable organic chemicals, cor process development, preliminary
Employs—10

Specialty Paper Box Co

(a Corp)
6310 Avalon Blvd Los Angeles
(213) 232-1211
SIC 2652 Estab. 1932
Pres Max R Ginsburg
Gen Mgr Sec Treas William V
Plant Mgr Frank Cross
Sales Mgr Martin S Randles
Office Mgr Ann Gorman
Product—rigid paper boxes
Employs—125

Specialty Paper Mills Inc

8834 S Millergrove Dr
Santa Fe Springs 90670
(213) 692-8737 (213) 723-11
SIC 2631 Estab. 1961
Chrmn of Bd & Pres John A
V Pres in charge of Sales A
Exec V Pres & Gen Mgr Rone
V Pres Richard G Gabriel
Confr John B Day
Product—paper board manu corrugating medium, fourdr colored liner and specialty liner and specialty papers

Specialty Pipe & Tube Co of Inc

3711 Long Beach Blvd Long
(213) 595-5593
SIC 3317 Estab. 1972
Pres Leonard Baroff
V Pres Joel Klausner
Sec Stuart Krueger
Treas Peter Davidson
Gen Mgr Robert S Fischbeck
Product—pipe & tubing
Employs—5
Branch: Specialty Pipe & Tu. Ohio

Specialty Truck Body Inc

(PO Box 2286) 1036 N 11th
San Jose 95106
(408) 295-7750
SIC 3713 Estab. 1945
Pres Al Davidson
Product—truck bodies
Employs—12

Specification Chromlum Cori

(PO Box 2885) San Rafael 94
712 Francisco Blvd San Rafael
(415) 456-3753
SIC 3471 Estab. 1956
Pres Richard Kilmurray
Product—anodizing and plating
Employs—12

Spec Plastics Inc

7224 Atoll Ave North Hollywood
(213) 982-0300
SIC 3079 Estab. 1968
Pres & Gen Mgr Thomas W F
V Pres Lisa L Reid
Sec-Treas Betty Reid
Chief Eng Andris Prieditis
Product—plastic hardware
Employs—42

Spec Tool Co

(PO Box 1056) 9626 E Beve
Pico Rivera 90660
(213) 723-9533
SIC 3550 Estab. 1953
Pres A G Fink
V Pres & Gen Mgr Al Fink Jr

SOUTHERN CALIFORNIA
Business Directory and Buyers Guide
1980 EDITION

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Editor-Publisher



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Sepulveda 91343
(213) 892-0761
M. Weinburg, PRES
Nand K. Aggarwal, GEN MGR
Wilmina Hill, FIN
Kathryn Puhl, SALES
Debra Morehouse, PA
Ben Weinberg, MFG
Transformers
Coils
SIC: 3610, 3621
EMP. 35 C H E M

PTI CONTROLS
1818 E. Orangethorpe
Fullerton 92631
(714) 871-4941
David E. Bauer, PRES
Transformers
Power Supplies
SIC: 3610, 5063
EMP. 50 C H E M D

**QUALITY COMMUNICATIONS
INC**
2900 E. La Jolla Rd.
Anaheim 92806
(714) 630-7520
Robert T. Spaulding, PRES
Transformers
SIC: 3612
EMP. 10 C I E M

**RAYCO ELECTRONIC MFG.
INC.**
1625 12th St
Santa Monica 90404
(213) 450-0777
P. Patel, PRES
A. Patel, GEN MGR
B. Rose, MKT SALES
M. Patel, MFG
Transformers
Coils
SIC: 3610, 3621
EMP. 12 C H E M D S

RHOMBUS INDUSTRIES INC
15801 Chemical Lane
Huntington Beach 92649
(714) 898-0960
David Duke, PRES
Lorrana Rogers, GEN MGR
Kenneth Strano, SALES MGR
Transformers
SIC: 3610
EMP. 50 C H E M

SCINTILLA POWER CORP
209 Willis
Camarillo 93010
(805) 484-4361
C. C. O'Reilly, PRES
J. A. O'Reilly, MKTG
Carla Bauer, SALES
Tom Fitzgerald, PA
Ed Warner, PROD MGR
Transformers
SIC: 3610
EMP. 75 C H M

SIERRA TRANSFORMER CO
16625 Norwalk Blvd.
Cerritos 90701
(213) 926-3345
H. T. Coffee, PRES
E. Esparza, SALES MGR
Transformers
SIC: 3612
EMP. 100 C I E M

SPATRON, INC.
2468 Mariondale Ave.
Los Angeles 90032
(213) 227-6821
J. R. Singleton, PRES
H. P. Balderson, VP
J. W. Wardell, ENG
Transformers
Filters
SIC: 3610, 3569
EMP. 50 C H M

STANDARD INDUSTRIES
14250 Gannett St.
La Mirada 90638
(714) 523-2970
J. Ross Reed, PRES CEXO
H. Alderdice, FIN
P. G. Chaply, PL MGR MKT
Clarke Reese, SALES
Eugene Lawrence, PA
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Transformers
Coils
Magnetic Equipment
Coils, Toroidal
Electronic Assemblies
Power Supplies
SIC: 3610, 3679
EMP. 125 C H E M

**TELEDYNE CRITTENDEN
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INDUSTRIES**
711 Knox Ave.
Gardena 90248
(213) 321-4355
Roscoe M. Power, PRES
Transformers
SIC: 3610
EMP. 65 C H M

TOROIDAL COMPONENTS CO.
1374 E. Walnut St.
Pasadena 91106
(213) 795-7123
Jesse R. Watson, PAR
John Onisko, PAR
Transformers
SIC: 3610
EMP. 18 P H M

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Hank Kohnen, S MGR
Rodger Green, PA
H. Turney, VP MFG
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Rectifiers
Power Supplies
SIC: 3610, 3670
EMP. 82 C H M

**WESTLAKE MAGNETICS
INC.**
3139 Los Feliz Dr.
Thousand Oaks 91360
(805) 497-3835
Ronald Stanley, PRES
Motor Winding
Coils
Transformers
SIC: 3610
EMP. 26 S O H M
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**ZENITH TRANSFORMER CO.,
INC.**
1728 W. 130 St.
Gardena 90249
(213) 321-4551
H. C. Hornickel, PRES S MGR
B. B. Weiss, SEC TREAS GEN
MGR
S. Margolis, MFG
B. Coiffette, CE
Transformers
Filters
SIC: 3610, 3569
EMP. 50 C H M

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POWER HYBRIDS INC
1742 Crenshaw Blvd.
Torrance 90501
(213) 320-6160
Vahan Garboushian, PRES
W. Edward Naugler Jr., EVP
John M. Boujikian, TREAS
Wayne E. Schaub, MKTG MGR
Transistors
SIC: 3674
EMP. 100 C E M

POWER TRANSISTOR CO
800 W. Carson St.
Torrance 90502
(213) 320-1190
Chet Szczesney, PRES
Luis Howard, SALES MGR
Cheryl Mier, PURCH AGT
Transistors
SIC: 3674
EMP. 20 C E M

ROBISON ELECTRONICS INC
3580 Sacramento Dr.
San Luis Obispo 93401
P. O. Box Y
San Luis Obispo 93401
(805) 544-8000
John F. Robison, PRES
John Mac Donald, PURCH AGT
Transistors
SIC: 3674
EMP. 130 C E M

**SOLID STATE ELECTRONICS
CORPORATION**
15321 Rayen St.
Sepulveda 91343
(213) 894-2271
E. Politi, PRES
Transistors
Printed & Etched Circuits
SIC: 3674, 3679
EMP. 15 C H E M D

TRANSLATION SERVICES

AGNEW TECH-TRAN INC.
21050 Erwin St.
Woodland Hills 91367
(213) 340-5147
Irene Agnew, PRES
Translation Services
Audio Visual Programs
SIC: 7399, 7813
EMP. 30 C H S

**INTERNATIONAL
TRANSLATION BUREAU INC.**
125 W. 4th St., #240
Los Angeles 90013
(213) 629-1990
Mrs. America I. Thatcher
Translation Services
SIC: 7399
EMP. 2 C H S

**THE MITANI TRANSLATION
SERVICE**
321 E. 2nd St., Ste. 605
Los Angeles 90012
(213) 623-8447
Nellie Mitani, PRES
Translation Services
SIC: 7399
EMP. 10 P H S

**PIERCE ASSOCIATES
INTERNATIONAL
PIERCE CONSOLIDATED**
P. O. Box 4379
Irvine 92716
(714) 646-8815
A. M. Pierce, OWN
P. A. Moore, PERS
Translation Services
SIC: 7399
EMP. 75 S O H S

SOLLOS INC
2231 S. Barmelina Ave.
Los Angeles 90064
(213) 820-5181
Dr. Milo Macha, PRES
Translation Services
SIC: 7399
EMP. 10 C E M

TRANSMISSION EQUIPMENT

**ASSOCIATED DIESEL
SERVICE & EQUIPMENT**
P O Box 1212
Wilmington 90748
(213) 835-7254
Robert F. Kafka, PRES
Marine Diesel Engines
Gears
Diesel Engines & Parts
Transmission Equipment
SIC: 5084
EMP. 51 C H E D R S

A-S TRANSMISSION INC.
8747 Shirley Ave.
Northridge 91324
(213) 886-9406
Rachiel Adkins, PRES
R. Furman, VP MKT SLS
Transmission Equipment
SIC: 3710
EMP. 5 C H E M D S
See Our Advertisement

N. A. D'ARCY COMPANY
7404 S. Garfield Ave.
Bell Gardens 90201
(213) 773-5511
Chuck Whittington, PRES
David L. Ankeny, VP
Transmission Equipment
Brake Parts & Equipment
Protective Coatings
SIC: 5063, 5013, 5029
EMP. 30 C H I D

**DODGE MANUFACTURING
DIVISION**
DIVISION OF RELIANCE
ELECTRIC COMPANY
9500 Telstar Ave.
El Monte 91731
(213) 773-3251
C. W. Hosey, AR MGR
Transmission Equipment
SIC: 3710
EMP. 18 C M

EXHIBIT 3.H



A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 1—Historical Background; Carbon Tetrachloride and Tetrachloroethylene

Richard E. Doherty*

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Carbon tetrachloride (CTC), tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were four of the most widely used cleaning and degreasing solvents in the United States. These compounds were also used in a wide variety of other applications. The history of the production and use of these four compounds is linked to the development and growth of the United States' synthetic organic chemical industry, and historical events that affected the development and use of chlorinated solvents in general. Part 1 of this article includes a discussion of the historical background common to each of the four solvents, followed by discussion on the history of CTC and PCE. In the early years of the 20th century, CTC became the first of the four solvents to come into widespread use. CTC was used as a replacement for petroleum distillates in the dry-cleaning industry, but was later replaced by PCE. In the 1990s, CTC was phased out under the Montreal Protocol due to its role in stratospheric ozone depletion. © 2000 AEHS

Keywords: chlorinated solvents; TCE; PCE; TCA.

Introduction

Carbon tetrachloride (CTC), tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were four of the most widely used cleaning and degreasing solvents in the United States. These chlorinated solvents were useful to industry because of their rapid evaporation rates, their low flammability and reactivity, and their ability to quickly and efficiently dissolve a wide range of organic substances. In general, the largest historical end uses of these compounds were in vapor degreasing, metal cleaning, and dry-cleaning. As the usage of the four solvents evolved over time, one solvent often became popular for a particular application, only to be gradually replaced by one or more of the others. These four compounds have also been used in adhesives, pharmaceuticals, and textile processing; as extraction solvents, paint solvents and coating solvents; and as feedstocks for production of other chemicals. The widespread use and subsequent disposal of CTC, PCE, TCE, and TCA led to their being among the most commonly-found contaminants at hazardous waste disposal sites.

This discussion focuses on the history of the production and use of these four compounds, primarily in the United States. The histories of these chemicals are linked to the development and growth of the United States' synthetic organic chemical industry, and to historical events that affected the development and use of chlorinated solvents in general. Information on how these factors affected the common history of the

four solvents is therefore provided prior to focusing on their individual histories.

The United States' Synthetic Organic Chemical Industry

In many respects, the establishment of the synthetic organic chemical industry in the United States was a direct result of World War I. Prior to the war, raw materials and chemical technologies were generally imported to the United States from European countries, particularly Germany (Haynes, 1945a). Virtually no manufacturing of synthetic organic chemicals (other than those derived from coal tar) existed in the United States prior to World War I. Synthetic chemicals that were manufactured in the United States at this time, such as acetone, chloroform, ether, acetic acid, formaldehyde, acetaldehyde, amyl acetate, and vanillin (United States Tariff Commission, 1921) tended to involve relatively simple manufacturing processes.

The outbreak of World War I virtually halted European chemical exports to the United States, creating an immediate need for domestic sources of chemical raw materials, intermediates, and finished products. The rush to expand chemical production in the war years began in earnest. Strong legislation was enacted to assist United States production efforts, such as the Trading-with-the-Enemy Act of October 1917 that allowed confiscation of German plants and patents (Steen, 1995). By the end of the war in November 1918, the United States had developed the capacity to fulfill nearly all of its domestic demand for synthetic chemicals (United States Tariff Commission, 1921).

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In the years immediately following the war, however, a period of severe over-capacity ensued. The early 1920s saw operating losses and decreased production at nearly all major chemical companies (Dutton, 1949; Whitehead, 1968; Forrestal, 1977). The resumption of chemical imports after the war exacerbated the situation, causing the United States Government to institute steep tariffs and require importers to obtain import licenses, which could only be obtained in cases where domestic supplies were unsatisfactory (United States Tariff Commission, 1921).

By the late 1920s, the United States' synthetic organic chemical industry assumed major economic importance due in large part to the expansion of the lacquer and rayon industries, and the use of synthetic chemicals in products such as medicines, perfumes, flavors, rubber accelerators, photographic developers, explosives, and flotation agents. In 1928, sales of synthetic organic chemicals exceeded those from coal-tar-derived chemicals for the first time. Between 1921 and 1929, the production of synthetic organic chemicals increased from 21 million to over 633 million pounds (United States Tariff Commission, 1928; 1929).

Major Producers of Chlorinated Solvents

Although many companies produced one or more of the four chlorinated solvents, several merit individual discussion because of their pioneering role and/or longevity in the industry. The Dow Chemical Company of Midland, Michigan played a major role in the development and production of chlorinated solvents in the United States. Dow began operation in 1897 with the extraction of bromine and later chlorine from the brines below their Midland facility. The company's founder, Herbert Dow, initially used chlorine to make bleach, but by 1913, he began to exit the bleach business, believing that the future lay in producing other useful compounds from chlorine. Through an intensive research and development effort, Dow Chemical was to become one of the major developers and producers of chlorinated solvents in the United States with production facilities in Midland, Michigan; Freeport, Texas; Velasco, Texas; Pittsburg, California; and Plaquemine, Louisiana (Whitehead, 1968). The research work resulted in many advances, some unrelated to solvent applications. For example, the 1933 discovery of Saran (currently used as a food wrapping) was an inadvertent by-product of Dow's research into chlorinated dry-cleaning solvents.

Another major producer of chlorinated solvents, E. I. Du Pont de Nemours & Company (Du Pont), began operating in Wilmington, Delaware in 1804 as a gunpowder manufacturer. Until the very early 1900s, Du Pont's activities were limited to manufacture of gunpowder and explosives such as TNT. The company began diversifying through acquisition and enhanced research in the early 1900s (Du Pont, 1952). Du Pont's entry into the field of chlorinated solvents essentially began with the acquisition of the Roessler & Hasslacher Chemical Company (R&H) in 1930. The company then became the R&H Chemicals Department of Du Pont. R&H, operating out of Niagara Falls, New York, specialized in the electrochemical processes used in the production of chlorine and halogenated

chemicals. The R&H unit was responsible for the production of chlorinated compounds for use in electroplating, metal cleaning, bleaching, refrigeration, dry-cleaning, and other uses (Dutton, 1949).

The Warner-Klipstein Chemical Company (c. 1915-1928) and its successors Westvaco Chlorine Products Corporation (1928-1948), Food Machinery and Chemical Corporation (1948-1961), and FMC Corporation (1961-c. 1979) produced chlorinated solvents in South Charleston, West Virginia (Haynes, 1949; Chem. Eng. News, 1959a; United States Tariff Commission, 1921-1962). Warner-Klipstein was formed in 1915 as a joint venture between E. C. Klipstein & Sons and the Warner Chemical Company. During the 1930s, the Westvaco Chlorine Products Company was the largest producer of chlorine in the world (Haynes, 1945b). Westvaco and/or its successors also produced CTC, PCE, and TCE (United States Tariff Commission, 1921-1972).

Chlorinated Solvents in Dry-cleaning

Many colorful stories exist regarding the origins of dry-cleaning, ranging from accidental spillage of kerosene onto clothing to a French sailor falling into a vat of turpentine. What all the stories have in common is the discovery of how organic solvents almost magically removed dirt and grease from clothing. The earliest known dry-cleaner opened for business in Paris in 1840, but dry-cleaning establishments were not to reach the United States until near to the turn of the century (O'Hanlon, 1997).

Dry-cleaning fluids used in the early 1900s consisted almost entirely of gasoline, which was relatively quickly replaced by other petroleum distillates such as naphtha, kerosene, benzene, and Stoddard solvent (Chem. Tr. J. Chem. Eng., 1933; Dutton, 1949). Petroleum distillates presented several problems as dry-cleaning agents. Dry-cleaning was costly and slow, and clothes were left with a disagreeable odor. More importantly, the distillates were highly flammable. In the words of an industry spokesperson, dry-cleaning shops "tended to blow up a lot" (O'Hanlon, 1997). As a result, many cities adopted ordinances requiring dry-cleaners to locate away from highly populated areas. Despite these difficulties, the dry-cleaning industry was firmly established in the United States by 1919 (Dutton, 1949).

Although PCE is commonly known as a dry-cleaning solvent, TCE and CTC were widely used in dry-cleaning prior to the large-scale acceptance of PCE. These compounds resulted in a less expensive, faster, and safer dry-cleaning process and virtually eliminated the problem of disagreeable odors (Dutton, 1949). The chlorinated solvents also cleaned more effectively and were more easily reused.

In general, chlorinated solvents were used by small dry-cleaning shops, while the larger dry-cleaning plants continued to use petroleum-based cleaners such as Stoddard solvent and 140-F solvent (a naphtha fraction). These petroleum-based cleaners were significantly less expensive than their chlorinated counterparts, but were rarely recycled (Seiler, 1960). Due to the high volumes used by the large plants, and the lack of recycling, the consumption of petroleum solvents in

dry-cleaning exceeded that of chlorinated solvents until about 1962 (Chem. Eng. News, 1962, 1967a).

World War II and the Korean War

The onset of World War II, and the resulting difficulty in importing goods from overseas, created severe shortages in products and raw materials. In 1941, the United States Director of Priorities Donald Nelson placed rigid controls on CTC, TCE, PCE and ethylene dichloride (1,2-dichloroethane) through the issuance of Preference Rating Order M-41, which granted first priority to military orders. An intermediate priority was assigned to essential civilian uses including (among others) grain fumigation, fire extinguishing, and refrigerant manufacture. Dry-cleaning and other fumigation uses were assigned the lowest priority. The Order also required solvent manufacturers to set aside up to 5% of the total monthly volume produced in an emergency pool (Ind. Eng. Chem., 1941a).

Unlike the production glut that followed World War I, the post-World War II years saw continued high demand for chlorinated solvents and other chlorinated compounds. Despite record production levels, chemical producers could not satisfy the demand, resulting in shortages of chlorine and chlorinated solvents. The beginning of the Korean War in 1950 increased military demand, extending the shortages further, even as production continued to increase (Chem. Eng. News, 1951).

Environmental Regulations

In the late 1960s, public awareness of the environmental effects of industrial chemicals increased dramatically. Beginning at this time and continuing into the 1970s, the discovery and widespread publicizing of industrial disposal sites increased pressure for regulatory remedies. Concurrently, early studies on possible carcinogenic effects of synthetic organic compounds, including chlorinated solvents, began to appear in scientific journals. These developments led to the creation of the Environmental Protection Agency (EPA) and the passage of the Clean Air Act (CAA) amendments in 1970, and the passage of the Water Pollution Control Act in 1972.

In accordance with a 1976 settlement decree, the terms of which were incorporated into the 1977 Clean Water Act, EPA was required to publish Water Quality Criteria (WQC) for a specific list of 65 priority pollutants (Arbuckle *et al.*, 1991). The priority pollutant list specifically included CTC, PCE, and TCE; TCA was included under the heading of "chlorinated ethanes." Proposed WQC for CTC, PCE, and TCE were published in March 1979 (USEPA, 1979a), followed by TCA and other chlorinated ethanes in October 1979 (USEPA, 1979b). The WQC were finalized in 1980 (USEPA, 1980).

In an effort to provide "cradle-to-grave" regulation of wastes considered hazardous, Congress passed the Resource Conservation and Recovery Act (RCRA) in 1976. When the first RCRA regulations were promulgated in 1980, wastes of each of the four solvents were classified as hazardous under several categories. Category F001 applied to all four solvents when spent during degreasing. F002 applied to spent

TCE, PCE, and TCA. Each of the four solvents was listed on the "U" list, which applies to discarded commercial chemicals and chemical intermediates.

The November 8, 1984 Hazardous and Solid Waste Amendments (HSWA) required EPA to restrict the land disposal of untreated solvent (and other) wastes, and to revise the Environmental Pollutant (EP) toxicity criteria. The latter requirement resulted in the adoption of the Toxicity Characteristic Leaching Procedure (TCLP), which brought with it new hazardous waste classifications, including D019 for CTC, D039 for PCE, and D040 for TCE. The TCLP rule, first proposed on June 13, 1986, became mandatory on September 25, 1990 for large-quantity generators, and March 29, 1991 for small-quantity generators (USEPA, 1990). Although TCA was originally proposed to be included on the TCLP list, it was excluded from the final regulations due to its propensity to hydrolyze, forming products that were not adequately simulated by EPA's fate and transport model (Newton, 1990).

Under the "land ban," wastes containing specific compounds above regulatory limits could not be disposed of on land, unless first treated to meet technology-based treatment standards. On November 7, 1986, EPA issued its first final rule including treatment standards under the land ban. Spent solvent wastes, including those containing CTC, PCE, TCE, and TCA, were among those covered under this final rule, which became effective on November 8, 1986. The effective date was extended to November 8, 1988 for several categories of wastes and generators, including small quantity generators. For spent solvent wastes generated under a CERCLA response action or RCRA corrective action, the compliance date was extended to November 8, 1990 (USEPA, 1986).

The Comprehensive Environmental Response, Compensation & Liability Act (CERCLA), passed in 1980, established reportable quantities for spills for a variety of compounds, including each of the four chlorinated solvents. The Act also established the Superfund for cleanup of the nation's worst disposal sites. The four chlorinated solvents became some of the most widely detected contaminants at Superfund sites.

The Safe Drinking Water Act (SDWA), signed into law on December 16, 1974, mandated the establishment of drinking water regulations for public water supplies (Pontius, 1990). In an Advance Notice of Proposed Rulemaking published in the Federal Register on March 4, 1982, EPA listed each of the four solvents as compounds to be regulated in drinking water supplies (USEPA, 1982). On June 12, 1984, EPA proposed non-enforceable Maximum Contaminant Level Goals (MCLGs) for eight volatile organics including CTC, TCE, and TCA (USEPA, 1984). The MCLGs were finalized and enforceable Maximum Contaminant Levels (MCLs) were proposed for the eight compounds on November 13, 1985 (USEPA, 1985a, b). These MCLs, along with requirements for monitoring, analysis, and public notification of violations, were finalized on July 8, 1987, and became effective January 9, 1989 (USEPA, 1987). Meanwhile, SDWA amendments were signed into law on June 19, 1986, requiring EPA to establish MCLs and MCLGs for 83 contaminants, including PCE as well as the previously regulated solvents, no later than June 1989

(Pontius, 1990). The MCL for PCE was finalized on January 30, 1991 (USEPA, 1991).

The Clean Air Act and Ozone Depletion

The first Clean Air Act, passed in 1963, focused more on the study rather than the solution of air problems. It was the 1970 Clean Air Act Amendments that began the regulation of emissions of TCE and PCE due to their suspected role in increasing ground-level ozone and smog formation. As a result, many users turned to TCA, which was not regulated under the 1970 CAA, as an alternative degreasing solvent (Zahodiakin, 1990; Chem. Eng., 1993).

In June 1974, an article appeared in the journal *Nature* that warned of a potential ozone problem many miles higher in the atmosphere. The article, authored by University of California scientists Sherry Rowland and Mario Molina, theorized that the photolytic destruction of chlorofluorocarbons (CFCs) could cause a chain reaction in which stratospheric ozone would be destroyed (Molina and Rowland, 1974). This landmark work began a 15-year controversy over the regulation of CFCs (Roan, 1989). The CFCs in question included chemicals used in packaging and refrigeration, such as trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12). The CFC controversy was to have significant effects on each of the four chlorinated solvents discussed in this article.

International agreement of CFC control was first documented under the Montreal Protocol, signed by 43 nations in September 1987. This agreement was limited solely to CFCs. Amendments to the Protocol, signed in June 1990 in London, included CTC and TCA as additional ozone-depleting substances, and adopted phase-out dates of 2000 and 2005, respectively (USEPA, 1994a). Shortly after the London meeting, the United States Congress passed the 1990 Clean Air Act Amendments (CAAA). Title VI of the CAAA incorporated the provisions and requirements of the 1990 amendments, but included a more stringent interim reduction and an earlier phase-out date for TCA. On July 30, 1992, EPA issued regulations to comply with Title VI (USEPA, 1992). In November 1992, the Copenhagen Amendments to the Montreal Protocol were signed, requiring the complete phase out of emissive uses of several compounds, including TCA and CTC, as of January 1, 1996. Interim Deadlines called for an 85% reduction of CTC use (relative to 1989 levels) by 1995, and a 50% reduction in TCA use (relative to 1989 levels) by January 1, 1994. EPA proposed adoption of this accelerated phase-out schedule on March 18, 1993 (USEPA, 1993a), and finalized the schedule on December 30, 1993 (USEPA, 1993b).

On May 12, 1993, EPA issued a list of acceptable substitutes for TCA. The list, finalized on March 18, 1994 (USEPA, 1994b), included TCE and PCE, which, ironically, were two metal-cleaning compounds TCA largely replaced in the 1970s due to the original Clean Air Act.

The 1990 Clean Air Act Amendments listed each of the four solvents as Hazardous Air Pollutants (HAPs). The amendments required that the emission of HAPs be controlled through the promulgation of National Emission Standards, also known as NESHAPs. In

September 1993, the dry-cleaning industry became the first to be regulated under NESHAPs (USEPA, 1993c). In November 1993, EPA proposed NESHAPs for emissions of each of the four chlorinated solvents (among other chemicals) from halogenated solvent cleaning machines (USEPA, 1993d). On December 2, 1994, EPA promulgated the solvent cleaning NESHAPs with an effective date of December 1997 for large sources (USEPA, 1994c).

Carbon Tetrachloride (CTC)

CTC, also known by the various chemical and trade names listed in Table 1, was a widely used cleaner and solvent. Of the four chlorinated solvents discussed, it was the first to be produced in the United States and the first to come into general use. As a result, production and use data are available over a longer time span than for the other solvents discussed. A list of CTC manufacturers and their approximate periods of production is given in Table 2. CTC production data are shown in Figure 1.

Table 1. Synonyms for carbon tetrachloride

Chemical names	carbon chloride methane tetrachloride perchloromethane tetrachlorocarbon tetrachloromethane
Trade names	Carbona (<i>A. Klipstein & Co.</i>)* Benzinoform Flukoids Necatorina Refrigerant R10 R10 Tetrafinol Tetraform Tetrasol Univerm Vermestrocid

*Manufacturer names in italics.

Table 2. Major manufacturers of carbon tetrachloride

Company	Approximate period of manufacture
Allied Chemical & Dye	1955-1981
Brown Company	1925-1928
Diamond Alkali/Diamond Shamrock	1944-1986
Dow Chemical	1908-present
Eastman Kodak	1925-1927
E. I. Du Pont de Nemours	1974-1989+
Ethyl Corporation	1969-1977
Frontier Chemical/Vulcan Materials	1956-present
LCP	1981-1991
Mallinckrodt Chemical Works	1956-1960
Niagara Smelting/Staufier Chemical/Akzo	1922-1991
Occidental Chemical	1987-1994+
Pittsburgh Plate Glass/PPG Industries	1957-1972
Seeley & Company	1941-1943
Taylor Chemical	1933-1944
Warner Chemical/Warner-Klipstein/Westvaco	1908-1979
Chlorine/Food Machinery and Chemical/FMC Corp	

Sources include US Tariff Commission, 1921-1972; USITC, 1973-1994; and company Web sites.

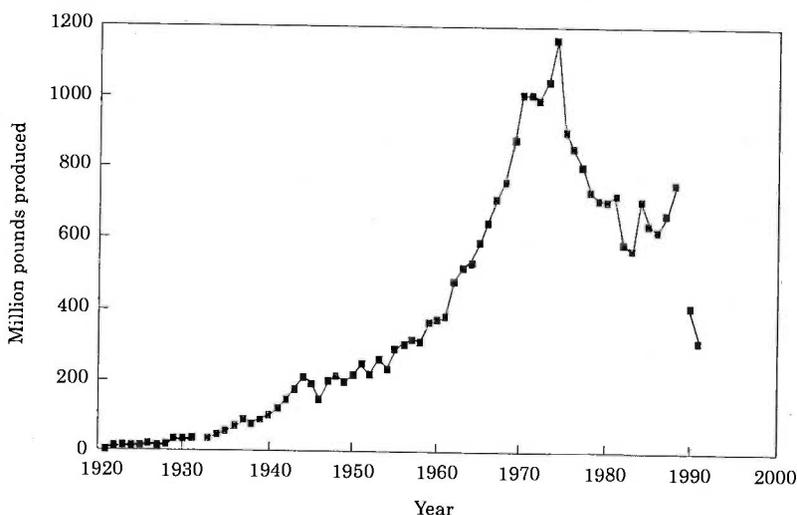


Figure 1. United States production of carbon tetrachloride (CTC).

Uses

Because of its relatively long history, CTC has seen a variety of uses. These are discussed below along with their corresponding time period of popularity. In addition to the uses discussed below, CTC was also used to render petroleum fractions nonflammable; as an azeotropic drying agent for spark plugs, as a delousing agent; and in dry/plasma etching, petroleum refining and pharmaceutical manufacturing. It was also used to extract oils from flowers and seeds, grease from bones and hides, and alkaloids from plants (Mellan, 1957; Merck, 1983). As a solvent, CTC was used in liquid chromatography, de-inking of paper, and the manufacture of rubber (EDF, 2000). CTC was used as a component of floor waxes, furniture polishes, paints, and varnishes (Mellan, 1957). As a metal degreasing solvent, CTC was at a disadvantage relative to other solvents because it left metal surfaces susceptible to corrosion (Kirk and Othmer, 1949).

Production methods

Prior to the 1950s, nearly all CTC produced in the United States was manufactured by the chlorination of carbon disulfide. This method, developed in 1893, remained in commercial use into the 1990s, typically aided by the use of a catalyst such as ferric chloride (Gregory, 1939; McKetta and Cunningham, 1979; Kroschwitz and Howe-Grant, 1991). In large-scale production, the reaction was often carried out in lead or lead-lined vessels (Thorpe and Whiteley, 1938; Kirk and Othmer, 1949). Among the plants that used the carbon disulfide process were the South Charleston, West Virginia facility operated by the Warner-Klipstein Chemical Company and its successors, including the Westvaco Chlorine Products Corporation (Haynes, 1949; Chem. Eng. News, 1959a).

Beginning in the 1950s, CTC production through the pyrolytic chlorination of hydrocarbons such as methane or propane became more popular (Kroschwitz and Howe-Grant, 1991). This process, often

referred to as chlorinolysis, produced PCE as a by-product. A variation of this process, involving the photochemical chlorination of methane, was discussed in a 1954 patent assigned to the Diamond Alkali Company (Chem. Week, 1954; Skeeter and Cooper, 1954).

As of 1975, the breakdown of production processes was as follows: the methane chlorination process accounted for 55% of total production, and was used by Allied Chemical, Dow, Du Pont, FMC Corporation, Stauffer Chemical, and Vulcan Materials. The carbon disulfide process accounted for 30% of production, and was used by FMC and Stauffer. The propane chlorination process accounted for 15% of production, and was used by Dow, Stauffer, and Vulcan (Khan and Hughes, 1979). The latter process is believed to be the subject of Dow's 1960 patent infringement suit against Stauffer Chemical. In an out-of-court settlement, Stauffer paid Dow a \$1.5 million licensing fee for the use of this process (Chem. Eng. News, 1960a, 1961).

CTC can also be produced through the oxychlorination of hydrocarbons, although this process was primarily used overseas. Producers of methylene chloride and chloroform also produce small quantities of CTC as a by-product (Kroschwitz and Howe-Grant, 1991).

In the early-to-mid 20th century, producing plants would often produce CTC when they had a surplus of chlorine gas and desired to convert it into a product that was more easily stored for future use. CTC production was therefore often intermittent during these years, and was dependent upon the availability of surplus chlorine (Ind. Eng. Chem., 1941b).

Technical grades of CTC can contain less than 1 part per million of carbon disulfide if produced by carbon disulfide chlorination, as well as trace amounts of bromine, chloroform, and hydrochloric acid. Although many commercial formations contained no corrosion inhibitors, those that did typically contained chemicals such as alkyl cyanamids, diphenylamine, ethyl acetate, and ethyl cyanids (McKetta and Cunningham, 1979; Kroschwitz and Howe-Grant, 1991).

History of use

CTC was first prepared by Regnault in 1839 using the action of chlorine on chloroform in sunlight. During the 1890s, CTC was being produced in Germany, and England's United Alkali Corporation was investigating commercial-scale production. CTC was reportedly first brought to the United States in 1898 from Germany by Ernest C. Klipstein, who had secured exclusive rights to the sale of imported CTC. Klipstein sold CTC as a dry-cleaning and spot-removing agent under the trade name Carbona, in an attempt to disguise the chemical origin of the solvent. Carbona became an enormously popular cleaning agent over the following eight years (Haynes, 1945b; Kroschwitz and Howe-Grant, 1991).

1900–1920. CTC was probably first manufactured in the United States by Dow Chemical in about 1900. In that year, Dow sold five drums of CTC to the Larkin Soap Company for use as a nonflammable cleaning fluid (Haynes, 1954). The first commercial-scale production in the United States appears to have been in 1902, when the Warner Chemical Company of Carteret, New Jersey produced about 15,000 pounds (Kirk and Othmer, 1949). Another source cites 1905 as the year when Warner purchased process equipment and began CTC production (Trescott, 1981).

In 1903, Herbert Dow was manufacturing chloroform from CTC (Haynes, 1949; Whitehead, 1968). By 1909, however, problems with the process had cost Dow's Midland Chemical Company a good deal of time and money with little in the way of results (Whitehead, 1968). According to several sources, large-scale production of CTC began in the United States around 1907, but specific companies are not mentioned (Kroschwitz and Howe-Grant, 1991; NIH, 1999). Other more specific references indicate that 1908 was the year when Warner Chemical and Dow Chemical began production on a large-scale basis (Haynes, 1949; Kirk and Othmer, 1949). Dow's CTC sales in 1908 were 400,000 pounds (Trescott, 1981).

Dow doubled its production capacity to 150,000 pounds per month in 1910 as CTC became accepted as a household cleaning agent and fire extinguisher (Whitehead, 1968). By 1914, annual production had reached nearly 10 million pounds, much of which was used in dry-cleaning and fire extinguishers (Kroschwitz and Howe-Grant, 1991). The use of CTC as a solvent for rubber was also being explored at this time (Haynes, 1945b).

As CTC became a more successful product, the manufacturing scene changed. In 1915, E. C. Klipstein & Sons and the Warner Chemical Company merged to form the Warner-Klipstein Chemical Company. The merger was driven by Warner's CTC capacity satisfying Klipstein's need for a domestic source of CTC (for Carbona) due to the cutoff of German imports. Great Western Electro-Chemical Company began CTC production in Pittsburg, California in 1917. The Brown Company of Berlin, New Hampshire, a paper manufacturer that operated electrolytic cells to produce chlorine for paper bleaching, began CTC manufacture in 1919 as a means of converting excess chlorine and carbon disulfide into useful products (Haynes, 1945b, 1949).

Fumigation of stored grains with CTC began before World War I, but was greatly advanced by techniques and products developed during the war. During World War I, United States CTC production expanded significantly, but military demand exceeded production by more than 2 to 1 (Haynes, 1945b, 1954). During the war, CTC was used as a solvent and an intermediate in the manufacture of other chemicals, and as a solvent in the rubber industry. An estimated 10 million pounds were used to make chlorobromomethane smokescreens for military use (Brandt, 1997). Dow Chemical's wartime production totaled 22.9 million pounds (Whitehead, 1968).

1920–1930. As of 1921, CTC was produced in significant quantities by three United States firms: Dow Chemical, Great Western Electro-Chemical, and Warner-Klipstein. In 1922, Niagara Smelting of Niagara Falls, New York began production using the carbon disulfide process (United States Tariff Commission, 1921, 1922). Four years later, Stauffer Chemical entered the CTC business by purchasing Niagara Smelting's facility. Stauffer assumed full control of Niagara Smelting in approximately 1930 (Haynes, 1948).

CTC's principal uses in the 1920s were as a dry-cleaning solvent and a fire extinguisher (USGPO, 1920; United States Tariff Commission, 1925). The use of CTC as a fire extinguisher was the subject of considerable attention in the 1920s and 1930s due to CTC's ability to produce toxic phosgene gas when heated in the presence of moisture. Additives such as ammonia, organic phosphates, oils and fats were used in some formulations to prevent the formation of phosgene (Thorpe and Whiteley, 1938).

In approximately 1921, Dr Maurice Hall of the United States Department of Agriculture discovered that CTC successfully treated hookworm in domestic animals. Later, the treatment was extended to humans (mostly in the tropical regions), also with great success. A 1924 article reported that bauxite miners in British Guiana showed almost immediate improvement in their condition after CTC treatment, and that CTC was "infinitely more satisfactory from every point of view" relative to previously tried methods (Ind. Eng. Chem., 1924).

CTC was also used in the manufacture of many other chemicals, including CFCs, the production of which began in October 1929 at a small facility owned by Du Pont and General Motors (Ind. Eng. Chem., 1941c; Roan, 1989). The manufacture of CFCs was later to be termed "by far the most important application for CTC" (Kroschwitz and Howe-Grant, 1991). Other uses of CTC during the 1920s were as an industrial solvent and an insecticide component (Chem. Met. Eng., 1927). It was also used as a minor component of one of the first anti-knock gasoline formulations (Haynes, 1948).

1930–1938. The early 1930s saw CTC become commonly used for dry-cleaning (Chem. Tr. J. Chem. Eng., 1933). According to one source, PCE overtook CTC as the leading dry-cleaning solvent in 1934 (Kroschwitz and Howe-Grant, 1991), but the majority of sources place the date in the late 1940s (Chem. Week, 1953a;

Gerhartz, 1986; HSIA, 1994). During the 1930s, CTC also began to replace ether as a solvent, due to its equal or better performance and lack of fire hazard (Jones, 1931). For the same reasons, CTC had largely replaced benzene and acetone as solvents in the lacquer industry by 1938. However, the availability of TCE in the 1930s was already causing reduced demand for CTC as a cleaning solvent (Thorpe and Whiteley, 1938).

In 1938, six companies reported CTC manufacture to the United States Tariff Commission: Dow Chemical, Great Western, Niagara Smelting, Westvaco Chlorine, Taylor Chemical, and one unidentified company (United States Tariff Commission, 1938). However, a survey conducted by a trade journal yielded the names of four additional manufacturers: J. T. Baker Chemical, Diamond Alkali, Du Pont and Pennsylvania Salt Manufacturing Company (Chem. Met. Eng., 1939). In December 1938, Dow purchased Great Western, reducing the number of United States manufacturers to approximately eight (Whitehead, 1968).

1938–1950. In the years prior to World War II, CTC began to be replaced as a dry-cleaning and degreasing solvent by PCE and TCE (Grayson and Eckroth, 1979). The major factors contributing to this trend were (1) the higher toxicity of CTC, (2) the lack of an adequate recovery method for CTC, and (3) the need to ship CTC in galvanized, tin, or lead-lined containers due to its action on common metals such as steel (Chem. Week, 1953a; Kirk and Othmer, 1949). In contrast, TCE and PCE were easily recoverable due to low boiling points and narrow boiling ranges, and could be shipped in steel containers.

Despite decreased CTC use in dry-cleaning and degreasing, CTC production increased during World War II, partly due to its lower price relative to TCE and PCE, but largely due to heavy CFC use by the military (Ind. Eng. Chem., 1941c; Kirk and Othmer, 1949). The World War II years marked the starting point of CTC's large-scale use as a feedstock for CFCs. To meet this growing market demand, Dow Chemical's Texas division built a CTC facility in 1943. By 1947, CTC was among the company's major products (Whitehead, 1968).

By the late 1940s, CTC had been largely replaced as a dry-cleaning solvent by PCE. In 1948, only 33% of chlorinated dry-cleaning solvent was CTC as opposed to 60% PCE. By 1950, the ratio of PCE to CTC use in dry-cleaning was 3 to 1 (Kroschwitz and Howe-Grant, 1991).

1950–1960. Despite CTC's decreased usage in dry-cleaning and metal degreasing, overall production continued to climb in the 1950s. The increase was driven by the rapid expansion in the use of CFCs, and the rapid expansion of the chemical industry in general. By 1954, about half the total CTC demand was for CFC production, and roughly a quarter was for use in fire extinguishers. Metal cleaning, grain fumigation, and dry-cleaning accounted for roughly 15, 7, and 5% of production, respectively (Chem. Week, 1953a; Kroschwitz and Howe-Grant, 1991). In 1953, Dow Chemical began operation of a new PCE and CTC production facility in Freeport, Texas (Chem. Week, 1953b). Dow constructed a new CTC, PCE, and TCE

facility in Plaquemine, Louisiana between 1956 and 1958 (Chem. Eng. News, 1958).

1960–1970. CTC use continued to accelerate in the early 1960s due to its use in CFC production, particularly CFC-11 and CFC-12, and in its increased use as a grain fumigant. Between 1960 and 1969, CTC use grew at an annual average rate of 10.7%. However, by 1962, estimated use had decreased to only about 15 million pounds for solvent applications and about 2 to 3 million pounds in dry-cleaning. In 1962, seven United States companies produced CTC, including Dow Chemical, Allied Chemical, FMC Corporation, Pittsburgh Plate Glass Company, Stauffer Chemical and the Frontier Chemical division of Vulcan Materials. Stauffer Chemical was a major producer, with large facilities in Niagara Falls, New York, and Louisville, Kentucky. In 1963, Stauffer announced plans for a third plant in Le Moyne, Alabama, with a capacity of 70 million pounds per year (Chem. Eng. News, 1963a). The following year, the company announced plans to expand the Louisville plant by 20% (Chem. Eng. News, 1964a). In 1966, Vulcan Materials was expanding CTC capacity in Wichita, Kansas, and announced plants to expand in Geismar, Louisiana (Chem. Eng. News, 1966a; 1966b). Two years later, the company competed a plant expansion in Newark, New Jersey (Chem. Eng. News, 1968a).

CTC suffered a setback in early 1968 when the Food and Drug Administration moved to ban interstate commerce of the chemical and products containing it. The Food and Drug Administration believed that CTC posed a hazard when present in homes, and when used in products such as fire extinguishers (Chem. Eng. News, 1968b).

1970–1980. CTC use peaked in the early 1970s, with annual production exceeding one billion pounds. As of 1971, 80% of CTC produced went into making CFC-11 and CFC-12 (Lowenheim and Moran, 1975). By 1974, this percentage had increased to 95% (Chem. Mktg. Rep., 1975). Although its use as a degreasing and dry-cleaning solvent was negligible, its use as a fire extinguisher had increased, and it was still widely used in grain fumigation (McKetta and Cunningham, 1979).

CTC production began an uneven decline in the mid-1970s. In 1970, CTC was officially banned from all United States consumer goods due to its toxicity (Kroschwitz and Howe-Grant, 1991). Studies identifying CTC as an animal carcinogen began to appear in 1972 (NIH, 1999). Rowland and Molina published their findings implicating CFCs in stratospheric ozone depletion in 1974, and a ban on CFCs in aerosol products went into effect in October 1978 (Roan, 1989).

As of 1978, ten CTC plants remained in production in the United States. The largest plants at this time were Du Pont's Corpus Christi, Texas facility (with an annual capacity of 372 million pounds) and FMC's South Charleston, West Virginia facility (272 million pounds) (Grayson and Eckroth, 1979). Du Pont's plant came on line in 1974, but as of 1975 was believed to be running well below capacity (Chem. Mktg. Rep., 1975). FMC's facility ceased CTC production in 1979 after over 50 years of operation. The closure was agreed to by

FMC as part of a plan approved by a Federal court judge in 1977. In exchange for ceasing CTC production, the company was allowed to utilize a less expensive system for alleviating CTC discharges to the Kanawha River (Chem. Eng., 1977). Largest among the remaining producers was Dow Chemical, which operated three plants with a combined capacity of 308 million pounds per year (Grayson and Eckroth, 1979). In 1976, Vulcan Materials announced plans for a new chloroform, methylene chloride and CTC facility in Wichita, Kansas, to be operational in 1978 (Chem. Eng. News, 1976). However, it should be noted that this plant was probably not intended to be a major producer of CTC; rather, CTC is routinely produced as a relatively minor by-product in the production of methylene chloride and chloroform (Kroschwitz and Howe-Grant, 1991).

1980–1990. The Resource Conservation and Recovery Act, passed in 1976 and implemented in 1980, regulated two categories of CTC wastes as hazardous: discarded commercial chemicals (U211), and spent degreasing solvent (F001). The use of CTC as a grain fumigant was banned in 1985 under the Federal Insecticide, Fungicide, and Rodenticide Act (NIH, 1999). Dow had exited the fumigation business three years earlier, leaving Stauffer Chemical and Vulcan Materials as the remaining producers (SRI International, 1985). The MCL for CTC, proposed in November 1985, was finalized in July 1987 and became effective in January 1989 (Pontius, 1990).

CTC demand continued to weaken in the early 1980s due to both ozone concerns and economic recession. The over-capacity in the CTC market as of 1982 was described as "monumental" (Chem. Mktg. Rep., 1983). Dow closed its 135 million pound CTC plant in Freeport, Texas in 1984. In about 1985, Stauffer decreased production in Louisville, Kentucky while expanding its plant in Le Moyne, Alabama. In 1986, Diamond Shamrock ceased CTC production, and Du Pont largely completed the conversion of its CTC facility to allow chloroform production (USITC, 1986; Chem. Mktg. Rep., 1986a). As of 1987, the number of companies producing significant quantities of CTC had been reduced to five. Although Dow and Vulcan Materials each operated two plants, the high-capacity Akzo plant in Le Moyne, Alabama (the former Stauffer plant) made it the leading producer as of this time (Kroschwitz and Howe-Grant, 1991).

1990–2000. By the early 1990s, CFC production accounted for 98% of total CTC demand (Chem. Mktg. Rep., 1992a). In 1990, CTC was designated as one of 189 Hazardous Air Pollutants under the Clean Air Act amendments. Also in 1990, with the implementation of the TCLP rule, CTC wastes subject to leaching were classified as hazardous (D019).

In 1991, Akzo and LCP closed their plants and exited the CTC business. Dow shut down its Pittsburg, California facility, leaving the Plaquemine, Louisiana plant as the country's largest. Only Dow, Vulcan, and Occidental remained as CTC producers as of 1992 (Chem. Mktg. Rep., 1992a; USITC, 1992).

The large-scale use of CTC virtually ended with its phase-out under the Montreal Protocol, implemented in the United States via the 1990 CAA amendments.

CTC's emissive use was directly banned as of January 1996. Its use as an intermediate was not; however, its primary use as an intermediate was in the production of CFC-11 and CFC-12, which were themselves banned as of the same date. Major users of CTC as an intermediate in the 1990s included Allied Signal, ICI, and Du Pont (Chem. Mktg. Rep., 1993). Its use as a solvent was estimated at only 2% of total production as of 1995 (Chem. Mktg. Rep., 1995). The 1992 amendments to the Montreal Protocol included a complete ban on the production and use of CTC as of January 1, 2000.

Tetrachloroethylene (PCE)

Tetrachloroethylene is most commonly known for its wide use in the dry-cleaning industry, but it has seen other important uses as well. Various chemical and trade names for PCE are shown in Table 3. A list of PCE manufacturers and their approximate periods of production is shown on Table 4. PCE production data are shown in Figure 2.

Table 3. Synonyms for tetrachloroethene

Chemical names	carbon bichloride carbon dichloride ethylene tetrachloride perchloroethylene tetrachloroethylene
Trade names	Ankilostin Blacosolve No. 2 Dee-Solv Didakene DowPer (<i>Dow Chemical</i>)* Isoform (<i>Dow Chemical</i>) Midsolv Nema Perclene (<i>Du Pont, Diamond Shamrock</i>) Perclene TG (<i>Du Pont, Diamond Shamrock</i>) Percosolv Per-Ex Perklone (dry-cleaning) Perm-A-Kleen Per Sec (<i>Vulcan Materials</i>) Phillsolv Tetracap Tetravcc Tetropil Wecosol (<i>Westinghouse</i>)

*Manufacturer names in italics.

Table 4. Major manufacturers of tetrachloroethylene

Company	Approximate period of manufacture
Diamond Alkali/Diamond Shamrock	1950–1986
Dow Chemical	1923–present
E. I. Du Pont de Nemours	1933–1986
Ethyl Corporation	1967–1983
Frontier Chemical/Vulcan Materials	1958–present
Hooker Chemical/Occidental Chemical	1949–1990
Hooker-Detrex/Detrex Chemical	1947–1971
Pittsburgh Plate Glass/PPG Industries	1949–present
Stauffer Chemical	1955–1985
Westvaco Chlorine	1940–1945

Sources include US Tariff Commission, 1921–1972; USITC, 1973–1994; and company Web sites.

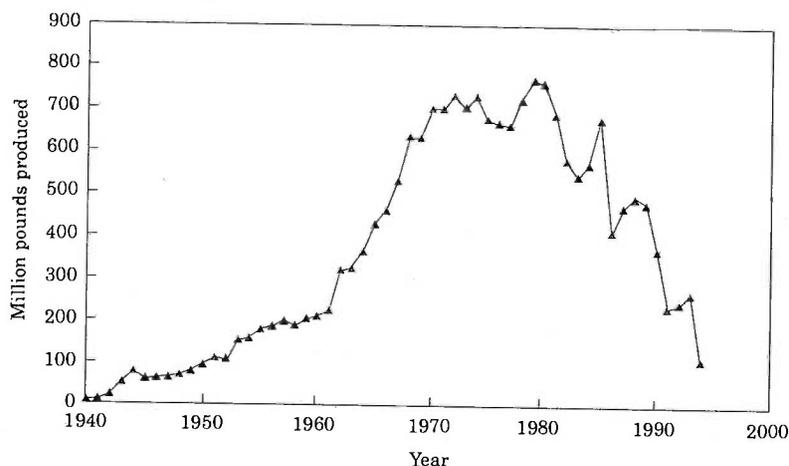


Figure 2. United States production of tetrachloroethylene (PCE).

Uses

Until approximately 1996, the highest-volume use of PCE was as a cleaning fluid by the dry-cleaning industry (Leder, 1999). Dry-cleaners favored PCE because of its relatively low toxicity, good cleaning properties, nonflammability, high stability, and moderate cost. As a metal cleaning and degreasing solvent, PCE was preferred for aluminum cleaning because of its high stability (Gerhartz, 1986), and for melting of wax and resin residues because of its high boiling point (HSIA, 1994). It was considered well-suited for sulfur recovery, rubber dissolution, paint removal, printing ink bleeding, soot removal, catalyst regeneration and electroplating pre-cleaning operations (Lowenheim and Moran, 1975).

In the textile industry, PCE was used as a carrier medium for fabric finishes, a scouring solvent for double knits, in sizing/desizing operations, and for spot removal of spinning oils and lubricants. As a chemical intermediate (PCE's primary use after 1996), it was used in the production of fluorinated compounds including CFC-113 and HFC-134a. PCE has also been used as a treatment for hookworm and some trematodes, as a replacement for PCBs in electrical transformers, and an ingredient in aerosol formulations. In small quantities, PCE has served as a carrier for rubber coatings, solvent soaps, printing inks, adhesives, sealants, polishes, lubricants, and silicones. Consumer products with PCE included typewriter correction fluid and shoe polish (Lowenheim and Moran, 1985; Merck, 1983; HSIA, 1994; USEPA, 1994d).

Manufacturing processes

PCE was typically manufactured as a co-product with either TCE or CTC. One of the earliest manufacturing methods was a multi-step process beginning with the chlorination of acetylene, followed by lime dehydrochlorination and chlorination steps (Seiler, 1960). This method, which yielded TCE as a co-product, gradually became obsolete in the 1970s due to the high price of acetylene. Hooker Chemical closed down the last plant

to use this process in 1978 (Kroschwitz and Howe-Grant, 1991).

More recent processes include (1) the high-temperature chlorination of ethylene or 1,2-dichloroethane (with TCE as a co-product), (2) the chlorinolysis of light hydrocarbon feedstocks (e.g. propane) or their partially chlorinated derivatives (with a CTC co-product), and (3) the oxychlorination of ethylene or C_2 chlorinated hydrocarbons (with a TCE co-product) (Kroschwitz and Howe-Grant, 1991). A high-temperature chlorination process was patented by Diamond Alkali (later Diamond Shamrock) in the early 1950s. Dow Chemical also used this process at its Freeport, Texas facility. The chlorinolysis process was developed in the 1940s and early 1950s. As of 1975, 44% of PCE was produced through chlorinolysis of propane, 35% by chlorination of 1,2-dichloroethane, and 3% by chlorination of acetylene (Khan and Hughes, 1979). PCE production by the chlorinolysis of propane was first used by Dow Chemical and later by Stauffer Chemical and Vulcan Materials. The oxychlorination process was used by PPG Industries (Chem. Eng. News, 1950a; Chem. Eng., 1969; Gerhartz, 1986).

Unlike TCE and TCA, PCE is relatively stable and requires only minor amounts of stabilizing additives to prevent decomposition. Earlier stabilizers included amines and hydrocarbons (Seiler, 1960; Chem. Eng., 1961); more recent stabilizers include compounds such as morpholine derivatives (Gerhartz, 1986). In the presence of water, unstabilized PCE will slowly hydrolyze to form trichloroacetic acid and hydrochloric acid (Kroschwitz and Howe-Grant, 1991).

History of use

In 1821, Michael Faraday (1791–1867), who was later to become known for his work in physics and electrochemistry, made one of his first important discoveries by preparing PCE from the thermal decomposition of his newly-discovered hexachloroethane (Partington, 1964; Gerhartz, 1986). Regnault obtained PCE in 1840 through two different processes (Kirk and Othmer, 1949).

1900–1930. Industrial production of PCE reportedly began in the first decade of the 20th century, likely in an acetylene-based plant in Europe (Gerhartz, 1986). As of 1914, PCE was being manufactured in the United States as a by-product of CTC manufacture (India Rubber World, 1914). However, it was not until 100 years after Faraday's discovery that PCE would see significant industrial use in the United States. PCE first appeared in the United States Census of Dyes and Synthetic Organic Chemicals in 1922. The sole United States producer at this time was Carbide and Carbon Chemicals Corporation, the predecessor of Union Carbide, but the 1923 and 1924 listings show the sole manufacturer as Dow Chemical (United States Tariff Commission, 1922–1924).

1930–1950. Du Pont entered the PCE business in 1933 when its Niagara Falls facility was modified and expanded (United States Tariff Commission, 1933; Chem. Eng. News, 1970a). PCE was reportedly introduced to the dry-cleaning industry in the late 1930s (Seiler, 1960; HSIA, 1994). Although one source states that PCE overtook CTC as the predominant dry-cleaning solvent in 1934 (Kroschwitz and Howe-Grant, 1991), the majority of sources indicate that this did not occur until the late 1940s (Chem. Week, 1953a; Gerhartz, 1986; HSIA, 1994). PCE appealed to dry-cleaners as a nonflammable substitute for petroleum solvents and a less toxic substitute for CTC.

In the early 1940s, PCE was manufactured by Dow, Du Pont, and Westvaco Chlorine (United States Tariff Commission, 1940–1945). During World War II, large quantities of PCE were consumed for use as a military smoke screen (Kirk and Othmer, 1949). By 1948, PCE use in dry-cleaning had overtaken CTC; by 1950, PCE was leading CTC by a 3 to 1 margin (Chem. Week, 1953a).

1950–1960. The 1950s was a decade marked by expansion of PCE production capacity. In February 1950, the Columbia Chemical division of Pittsburgh Plate Glass Company began construction of a new PCE plant in Barberton, Ohio. Partial production began in November 1950 (Chem. Eng. News, 1950b). In 1952, Diamond Alkali was constructing a plant to produce PCE and other organic chemicals (Chem. Week, 1952). In 1953, Dow Chemical began operation of a new PCE production facility in Freeport, Texas (Chem. Week, 1953b). By the late 1950s, Dow's Texas division was producing enough PCE each month to clean 12,000,000 men's suits (Whitehead, 1968). Also in 1953, Hooker–Detrex, a joint venture between Hooker Electrochemical Company and Detrex Corporation, announced the expansion of its Ashtabula, Ohio PCE production facility (Chem. Week, 1953c). Dow constructed a new CTC, PCE and TCE facility in Plaquemine, Louisiana between 1956 and 1958 (Chem. Eng. News, 1958). In late 1958, Vulcan Materials of Wichita, Kansas began the manufacture of dry-cleaning and industrial grades of PCE (Chem. Eng. News, 1959b). As of 1959, Dow and Du Pont supplied about half the market for PCE (Seiler, 1960).

By the end of the 1950s, the rapid expansion together with a slowing economy and rising imports resulted in excess supply. PCE plants in the United

States were operating at about two-thirds of their estimated 300 million pound annual capacity. Approximately 14 million pounds were imported in 1959 (Chem. Eng., 1961).

As of 1952, 80% of PCE was used in dry-cleaning, and about 15% in metal cleaning (Chem. Week, 1953a). As of 1959, the estimated use pattern was little changed, with 76% used in dry-cleaning and 16% in metal cleaning. PCE's share of the total vapor degreasing market in 1959 was about 10% (Seiler, 1960).

1960–1980. By 1962, PCE was the dry-cleaning solvent of choice, even when compared to petroleum-based cleaners such as Stoddard solvent (Chem. Eng. News, 1962, 1967a). Dow Chemical was the leading producer as of 1961, with 120 million pounds of capacity at three plants (Freeport, Texas; Pittsburg, California; and Plaquemine, Louisiana). Other manufacturers, in order of capacity, were Du Pont (55 million pounds), Diamond Alkali (45 million pounds), Pittsburgh Plate Glass (35 million pounds), Stauffer Chemical (30 million pounds), Detrex Chemical (25 million pounds), Frontier Chemical (15 million pounds), and Hooker Chemical (10 million pounds) (Chem. Eng. News, 1962).

The dry-cleaning industry was responsible for about 90% of PCE consumption in 1962 (Chem. Eng. News, 1963b) and 88% in 1967 (Chem. Eng. News, 1967a). The trend toward wash-and-wear clothing temporarily slowed the growth of PCE use, but this was counterbalanced to some extent by the introduction of coin-operated dry-cleaning machines in the early 1960s (Chem. Eng. News, 1962, 1967a; Lowenheim and Moran, 1975).

PCE imports increased significantly in the late 1950s and early 1960s. Imports accounted for only 2.2% of total supply in 1957, but by 1961 they had increased to 11.5%, or 30 million pounds. In 1963, an estimated 56 million pounds were imported. In 1965, allegations of "dumping" by French firms (i.e. selling at prices below fair value in violation of the 1921 Anti-Dumping Act) were resolved when price revisions were promptly made by the importers (Chem. Eng. News, 1962, 1964b, 1965a, 1965b).

The 1960s and early 1970s saw accelerated expansion in PCE manufacturing capacity. In late 1960, Hooker Chemical began operation of a 10 million pound per year facility in Tacoma, Washington. By 1967, the company was constructing a 20 million pound facility in Taft, Louisiana (Chem. Eng. News, 1960b, 1966a, 1967a). In 1963, Pittsburgh Plate Glass announced plans to build a new PCE/TCE production facility in Lake Charles, Louisiana, to supplement the 35 million pound annual PCE output of its Barberton, Ohio facility (Chem. Eng. News, 1963c). By 1971, the company (renamed PPG Industries in the intervening years) announced plans to triple the capacity of the Louisiana facility (Chem. Eng. News, 1971). In 1964, Stauffer Chemical announced the expansion of its Louisville, Kentucky plant to 70 million pounds (Chem. Eng. News, 1964a, 1967a). In 1965, the Frontier Chemical division of Vulcan Materials announced the expansion of its methylene chloride and PCE plant in Wichita, Kansas to 30 million pounds (Chem. Eng. News,

1965c, 1967a). Vulcan started up another PCE plant in Geismar, Louisiana in 1968 (Chem. Eng. News, 1968c). In 1967, the Ethyl Corporation began production at a 50 million pound facility in Baton Rouge, Louisiana (Chem. Eng. News, 1967b). Ethyl expanded the plant's production in 1970 (Chem. Eng. News, 1970b). In 1967, Diamond Alkali announced plans to more than double PCE production at its Deer Park, Texas plant to bring total capacity to 100 million pounds (Chem. Eng. News, 1967a, 1967c). In 1970, Dow Chemical started up a new production facility in Pittsburg, California. The \$10 million plant was the largest PCE plant in the western United States at the time (Chem. Eng. News, 1970c).

In contrast to the rapid increase in production capacity, PCE use in dry-cleaning was beginning to decline. In 1959, it was estimated that the average neighborhood dry cleaner used 50 to 100 gallons of PCE per month. However, improvements in dry-cleaning equipment and vapor recovery systems greatly increased the efficiency of PCE use over the following decades. One 55-gallon drum of PCE cleaned about 500 pounds of clothing in 1959 (Seiler, 1960), about 8000 pounds of clothing in 1975, and about 16,000 pounds of clothing in 1993 (Kirschner, 1994).

In late 1970, Du Pont announced that it was phasing out production at its Niagara Falls facility, which began operation in 1925. The company cited uncertainty in the supply and price of acetylene, a major raw material used in the plant. Newer PCE plants used cheaper raw materials, giving their owners a competitive advantage over Du Pont. Du Pont agreed to allow competing producer Diamond Shamrock to use the Du Pont trade name of PCE (Perclene), and to continue to operate the Niagara Falls facility to supply Diamond Shamrock's needs until that company could expand its Deer Park, Texas facility (Chem. Eng. News, 1970a). Shutdown of other acetylene-based plants was to follow, ending with the closing of Hooker Chemical's plant in 1978 (Kroschwitz and Howe-Grant, 1991).

Comparison of PCE's pattern of use between 1972 and 1975 showed how quickly conditions were changing. Usage in dry-cleaning decreased from 75% to 63%, while usage in metal cleaning and degreasing increased from 7% to 14%. Use as a chemical intermediate (mostly in the production of CFCs 113, 114, 115, and 116) increased from 7% to 13%. Exports and other uses remained stable at about 10% (Chem. Mktg. Rep., 1973, 1976).

1980–1990. PCE use in the United States peaked in 1980. The major reasons for the subsequent decline in PCE use were the improvement in dry-cleaning equipment and vapor recovery, the growth in popularity of washable fabrics, and the effect of new environmental regulations. In 1980, spent PCE still bottoms were classified as a hazardous waste under RCRA. PCE wastes were also classified as hazardous as a component of spent degreasing solvents (F001), other spent solvents (F002), and as a U-listed waste (U210). As of 1985, it was estimated that 53% of PCE was used in dry-cleaning, 28% as an intermediate (mostly in the production of CFC-113), 10% in metal cleaning, 5% in

exports, and 4% in other uses (Chem. Mktg. Rep., 1986b).

In an attempt to find new uses for PCE, Diamond Shamrock combined its Perclene TG formulation with a Westinghouse additive to form Wecosol. This product began use as a replacement for PCBs in electrical transformers in mid-1981 (Chem. Week, 1982). The toxicity of PCE prevented this application from being highly successful relative to competing fluids such as mineral oil and silicones.

Decreased PCE use inevitably led to plant conversions and shutdowns. In October 1982, Ethyl Corporation exited the PCE business by shutting down its 50 million pound per year production facility. On June 1, 1985, Dow shut down its PCE/CTC plant in Freeport, Texas, removing 60 million pounds of annual production capacity from the market. Dow continued to produce PCE in Pittsburg, California, and Plaquemine, Louisiana. Also in 1985, Stauffer Chemical and Diamond Shamrock ceased PCE production, and Du Pont announced its departure from the PCE business by the conversion of its Corpus Christi, Texas facility to the production of chloroform (SRI International, 1985). Remaining manufacturers as of late 1986 included Occidental Petroleum, Dow, PPG, and Vulcan (National Safety Council, 1997).

1990–2000. As of 1990, PCE use in dry-cleaning or textile processing consumed about 50% of total production. About 25% was used as feedstock and 15% was used in metal cleaning and degreasing (HSIA, 1994). United States consumption of PCE in the dry-cleaning industry continued its long decline, decreasing approximately 70% between 1988 and 1998. In 1991, Dow shut down its 50-million-pound facility in Pittsburg, California, and Occidental Chemical closed its 180-million-pound plant in Deer Park, Texas (Chem. Mktg. Rep., 1992b). With Occidental's exit, the number of United States PCE manufacturers had decreased to three as of 1991: Dow Chemical (Plaquemine, Louisiana), PPG Industries, and Vulcan Materials (USITC, 1991). Vulcan closed its 25 million pound Wichita, Kansas plant in 1996, but continued PCE production in Geismar, Louisiana (Chem. Mktg. Rep., 1997).

In 1991, EPA set an MCL for PCE at 5 micrograms per liter, and an MCLG of zero (USEPA, 1991). In September 1993, the dry-cleaning industry became the first to be regulated under the 1990 CAA NESHAPs. This distinction is not necessarily reflective of PCE's toxicity relative to other HAPs; the prime factor was a citizen's suit that resulted in a Consent Decree forcing EPA to take regulatory action (USEPA, 1993c). Under the Toxics Release Inventory 33-50 program, EPA called for voluntary reductions of emission of PCE and 16 other chemicals. Target reductions were 33% by 1992, and 50% by 1995, relative to 1988 usage rates (Kirschner, 1994).

Like the other chlorinated solvents, PCE was affected by ozone protection regulations. Because PCE was used as a feedstock for production of CFC-113 (a banned CFC under the Montreal Protocol), overall production decreased further in the years preceding 1996. After the CFC phase-out, PCE was increasingly used as a feedstock for HFC-134a, a

replacement for CFC-12 in automobile air conditioning systems (Chem. Eng., 1995). PCE also saw limited use as a feedstock for CFC replacements HCFC-123, HCFC-141b and HCFC-142b (HSIA, 1994; Leder, 1999).

Prior to 1992, most states regulated PCE as a volatile organic compound (VOC) because of its suspected role as a precursor of ground-level ozone (HSIA, 1994). In October 1992, EPA proposed to exempt PCE from regulation as a VOC due to PCE's negligible photo-reactivity. EPA finalized the exemption in February 1996 via issuance of a final rule (USEPA, 1996).

Despite the increased regulations and the huge decline in use by the dry-cleaning industry, PCE remains the solvent of choice for 85 to 90% of approximately 30,000 current-day dry-cleaners and laundrers. Typical equipment used today recovers 95 to 99% of the PCE used in the dry-cleaning process (O'Hanlon, 1997).

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A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 2—Trichloroethylene and 1,1,1-Trichloroethane

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Carbon tetrachloride (CTC), tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were four of the most widely used cleaning and degreasing solvents in the United States. Part 2 of this article describes the history of TCE and TCA. TCE production in the United States began in the early 1920s. TCE was used as a replacement for petroleum distillates in the dry-cleaning industry, and became the solvent of choice for vapor degreasing in the 1930s. TCE's use as a degreaser decreased in the 1960s due to toxicity concerns and the increasing popularity of TCA. Significant TCA use began in the 1950s with the development of suitable stabilizer formulations. In the 1990s, TCA was phased out under the Montreal Protocol due to its role in stratospheric ozone depletion. © 2000 AEHS

Keywords: chlorinated solvents; TCE; PCE; TCA.

Trichloroethylene (TCE)

Trichloroethylene, also known by a variety of chemical and trade names (see Table 1), was a widely used degreasing solvent that achieved public notoriety for its role in contaminating drinking water wells in Woburn, Massachusetts in the 1960s. As of 1997, TCE was reported as being present at 852 of 1430 National Priority List sites, making it one of the most commonly found contaminants at Superfund sites (ATSDR, 1997). A list of TCE manufacturers and their approximate periods of production is shown in Table 2. TCE production data are shown in Figure 1.

Uses

Due to its effectiveness, noncorrosivity, nonflammability and ease of recycling, few solvents matched the performance of TCE in cleaning and degreasing. A wide variety of entities used TCE, including the electronics, defense, chemical, rail, automotive, boat, shoe, food processing, textile, and dry-cleaning industries. Although TCE works best on fats, grease, and waxes, it is also a powerful solvent for a large variety of natural and synthetic substances. TCE's industrial and commercial applications included use as a refrigerant, a low-temperature heat transfer medium, a freezing point depressant in CTC fire-extinguishers, an extraction agent in the decaffeination of coffee, and a cleaner for optical lenses. TCE was used as an ingredient in printing inks, elastomers, industrial paints, paint strippers, lacquers, varnishes, lubricants, pesticides, and adhesives (Kirk and Othmer, 1949; Huff, 1971;

USDHHS, 1975; Gerhartz, 1986; Kroschwitz and Howe-Grant, 1991).

A pharmaceutical grade of TCE saw use as a general anesthetic and as an analgesic in dental extractions, childbirth and other short surgical procedures (USDHHS, 1975). In veterinary medicine, TCE was used as an anesthetic for pigs, dogs, and cats, and as a disinfectant and detergent for minor wounds and surgical instruments. In agriculture, TCE was used in grain fumigant mixtures (Huff, 1971).

Consumer products that contained TCE included shoe polish, drain and pipe cleaners, household cleaners, spot removers, disinfectants, paint removers, wig cleaners, upholstery cleaners, deodorizers, typewriter correction fluid, adhesives, mildew preventives, and septic tank cleaners (Aviado *et al.*, 1976; Schaumburg, 1990; National Safety Council, 1997). Brand-name consumer products that contained TCE in the past include Du Pont Dry Clean, Dux Water Repellent, Instant Chimney Sweep spray, Lash Bath false eyelash cleaner, Sears Air Freshener, Sears Odor Neutralizer, and Triad metal cleaner and polish (Huff, 1971).

In the textile industry, TCE was used to scour wool, cotton, and other fabrics, and as a solvent in waterless dyeing and finishing operations. As a chemical intermediate, TCE was used in the production of polyvinyl chloride, chloroacetic acid, hydrofluorocarbons, pharmaceuticals, insecticides, fire-retardant chemicals, and fertilizer (Merck, 1983; Gerhartz, 1986; Archer, 1996; HSIA, 1996; National Safety Council, 1997).

Production methods

Each of the PCE production methods discussed in Part 1 of this article, with the exception of the

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Table 1. Synonyms for trichloroethylene

Chemical names	
1,1,2-trichloroethylene	
1,1-dichloro-2-chloroethylene	
1-chloro-2,2-dichloroethylene	
acetylene trichloride	
ethinyl trichloride	
ethylene trichloride	
trichloroethene	
Trade names	
Algylen	
Alka-Tri (industrial grade)	
Aramenth	
Blacosolv (industrial grade)	
Clorylen	
Ethyl Trichloroethylene (industrial grade)	
Ex-Tri (industrial grade)	
Gemalgene	
Germalgene	
Hi-Tri (<i>Dow Chemical</i>)*	
Narcogen	
Narcosoid	
NCI-C04546	
Neu-Tri (<i>Dow Chemical</i>)	
Nialk Trichlor MD (<i>Hooker Chemical</i>)	
Nialk Trichlor MDA (<i>Hooker Chemical</i>)	
Nialk Trichlor X-1 (<i>Hooker Chemical</i>)	
Nialk Trichlor-Extraction (<i>Hooker Chemical</i>)	
Nialk Trichlor-Technical (<i>Hooker Chemical</i>)	
Perm-A-Clor (<i>Hooker-Detrex Inc.</i>)	
Perm-A-Clor NA(<i>Hooker-Detrex Inc.</i>)	
Perm-A-Clor NA-LR (<i>Hooker-Detrex Inc.</i>)	
Phillex (industrial grade)	
Stauffer Trichloroethylene (<i>Stauffer Chemical</i>)	
Threthylene	
Triad-E (<i>Hooker-Detrex Inc.</i>)	
Tri	
Trichlor Type 113 (industrial grade)	
Trichlor Type 114 (industrial grade)	
Trichlor Type 115 (industrial grade)	
Trichlor Type 122 (industrial grade)	
Trichloran	
Trichloen	
Trichloroethylene Dual (industrial grade)	
Trichloroethylene Extraction Grade (industrial grade)	
Trichloroethylene-Degr. Gen. Solv. (industrial grade)	
Trichloroethylene High Purity (industrial grade)	
Triclene (<i>Du Pont, Diamond Shamrock</i>)	
Tri-Clenc (<i>Du Pont, Diamond Shamrock</i>)	
Triclene D (<i>Du Pont, Diamond Shamrock</i>)	
Triclene High Alkalinity (<i>Du Pont, Diamond Shamrock</i>)	
Triclene L (<i>Du Pont, Diamond Shamrock</i>)	
Triclene LS (<i>Du Pont, Diamond Shamrock</i>)	
Triclene MD (<i>Du Pont, Diamond Shamrock</i>)	
Triclene ME (<i>Du Pont, Diamond Shamrock</i>)	
Triclene Paint Grade (<i>Du Pont, Diamond Shamrock</i>)	
Triclene R (<i>Du Pont, Diamond Shamrock</i>)	
Triclene	
Triklone (industrial grade)	
Trilene (anesthetic grade)	
Triline	
Triman (anesthetic grade)	
Trimar	
Tri-Paint Grade (industrial grade)	
Trisan	
Trivec	
Tromex	
Vapoclean	
Vapoclor	
Westrosol	

*Manufacturer name in italics.

Table 2. Major manufacturers of trichloroethylene

Company	Approximate period of manufacture
Carbide & Carbon Chemicals	1922–1935
Diamond Shamrock	1969–1977
Dow Chemical	1921–present
Ethyl Corporation	1967–1983
Hooker-Detrex/Detrex Chemical	1947–1972
Hooker Chemical/Occidental Chemical	1956–1980
Niagara Alkali	1949–1955
Pittsburgh Plate Glass/PPG Industries	1956–present
R&H Chemical/E.I. Du Pont de Nemours	1925–1972
Westvaco Chlorine	1933–1949

Sources include *United States Tariff Commission, 1921–1972; USITC, 1973–1994; and company Web sites.*

chlorinolysis process, could also be used to produce TCE. In addition to the acetylene production method, developed between 1903 and 1905 in Austria, TCE was also produced by the chlorination or oxychlorination of ethylene or 1,2-dichloroethane. PPG Industries developed and patented a catalyst-assisted oxychlorination process (Chem. Eng., 1969). Due to high acetylene costs, production methods gradually shifted over time toward the ethylene/1,2-dichloroethane methods. Production from acetylene was estimated at 100% in 1949 (Kirk and Othmer, 1949), 85% in 1968, 51% in 1971 (USDHHS, 1975) and only 8% by 1976 (Kroschwitz and Howe-Grant, 1991). The acetylene process was no longer used after 1978.

Commercial grades of TCE include stabilizers to prevent breakdown due to acids, metals, oxygen, light, and/or heat. Unstabilized TCE is slowly auto-oxidized by air, and can decompose rapidly in the presence of aluminum (Kroschwitz and Howe-Grant, 1991). Because vapor degreasing involved contact with metals, sometimes at high temperatures, stabilization was critical to the proper performance of TCE. TCE stabilizer formulations generally included an acid acceptor to neutralize hydrogen chloride, a metal stabilizer to complex metal salts, and an antioxidant to retard formation of oxidation products. Concentrations of stabilizing chemicals in TCE generally ranged from 0.1 to 0.5%, but could range up to 2%.

The use of stabilizers in TCE dates back to at least the mid-1930s (Davidson, 1938). Prior to 1954, amines (e.g. trimethylamine, triethylamine, diisopropylamine) were the most popular acid acceptors used in TCE stabilizers. Amines neutralized acidic decomposition products and prevented further degradation, but once the amines were depleted, decomposition would occur. In 1954–1955, Du Pont introduced a nonalkaline, multi-component stabilizer formulation based on a pyrrole. Most competitors licensed the pyrrole formulation from Du Pont, or a similar neutral system from Westvaco, and the new formulations quickly replaced amines (Chem. Eng., 1961). Alcohols, esters, ethers, substituted phenols and epoxides such as butylene oxide and epichlorohydrin were also used as TCE stabilizers. Epichlorohydrin use was discontinued in the 1980s due to toxicity concerns (Kircher, 1957; Standen, 1964; Areher, 1984; Gerhartz, 1986; Kroschwitz and Howe-Grant, 1991). Analgesic grades of TCE contained 0.008 to 0.012% thymol as an anti-microbial

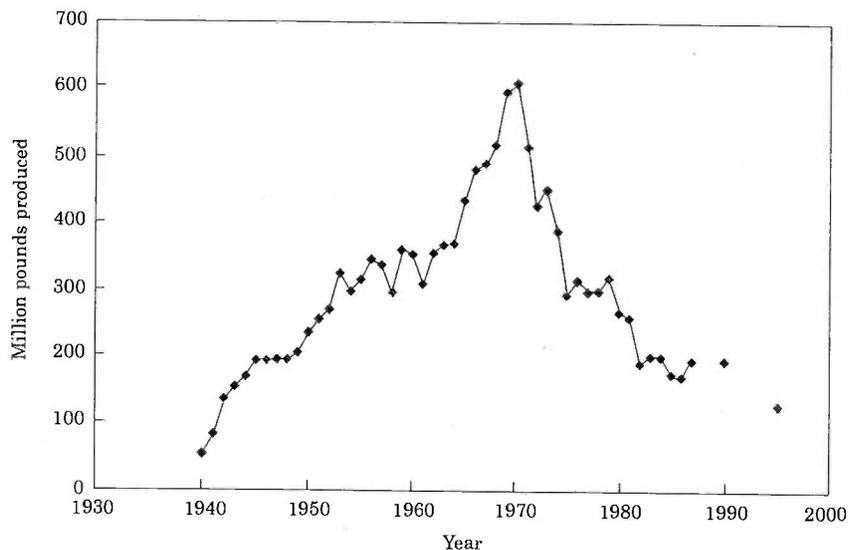


Figure 1. United States production of trichloroethylene (TCE).

agent, and were sometimes dyed with waxoline blue for identification purposes (Huff, 1971; Aviado *et al.*, 1976).

History of use

E. Fischer first prepared TCE in 1864 by the reductive dehalogenation of hexachloroethane (Fischer, 1864). However, little attention was given to TCE's use as a commercial chemical product until the early 1900s. The first TCE plant reportedly became operational in 1908 in Yugoslavia (Gerhartz, 1986). Production in Germany began in 1910 (Mellan, 1957).

In 1912 England's *Chemical Trade Journal* announced the introduction of a "new chlorinated carbon derivative". The new compound, TCE, was produced in two forms: one for laundries, and one for textiles and varnishes (Chem. Tr. J. Chem. Eng., 1912). One of TCE's other early uses was as an extraction agent for fats. TCE was thought to be ideal for this application because its low boiling point and narrow boiling range allowed nearly complete solvent removal from the resulting food products. However, as early as 1916, animal feeds containing soybean meal defatted with TCE were identified as the source of cattle poisoning. Extensive losses of cattle in Europe occurred between 1923 and 1925 from ingestion of TCE-defatted soybean meal (Huff, 1971).

1920–1930. In 1921, the production of TCE via the oxidation of acetylene in the presence of a mercuric catalyst was among a number of processes referred to as a field of "promising future development" (United States Tariff Commission, 1921). Although some sources cite 1923 or 1925 as the year when United States manufacturing of TCE began (USDHHS, 1975; Kroschwitz and Howe-Grant, 1991), the United States Census of Dyes and Synthetic Organic Chemicals indicates that Dow Chemical and the Carbide and Carbon Chemicals Corporation were manufacturing TCE as of 1921 and 1922, respectively (United States

Tariff Commission, 1921–22). In 1925, The Roessler & Hasslacher Chemical Company (R&H), previously a major importer of TCE, began domestic production at Niagara Falls, New York (Haynes, 1948).

Despite the existence of manufacturing capacity, TCE use was not industrially significant until the later 1920s. Earliest applications included use in boot polishes and printing ink dryers. The demand for TCE as a degreasing solvent was stimulated later in the 1920s by improvements in the metal degreasing process. As of 1927, the food processing industry was using TCE in "large and ever-increasing quantities" as an extraction solvent for natural fats and palm, coconut and soybean oils (Kroschwitz and Howe-Grant, 1991; Ind. Chemist, 1927). Medical use of TCE began in approximately 1928 with the treatment of trigeminal neuralgia (Oljenik, 1928).

1930–1940. Beginning in approximately 1930, TCE was one of the first chlorinated solvents (along with CTC) to be used in dry-cleaning as a substitute for the flammable petroleum distillates (Chem. Tr. J. Chem. Eng., 1933). TCE saw increased use in dry-cleaning of clothes as the decade progressed (Kroschwitz and Howe-Grant, 1991), and it was gaining market share from CTC in solvent applications (Thorpe and Whitely, 1938). In the mid-1930s, leading manufacturers of ferrous and non-ferrous metals began to use solvent degreasing equipment, including vapor, spray, and immersion degreasers. Stabilized forms of TCE were considered the best solvents for use in these degreasers (Davidson, 1938).

Although TCE was termed the "ideal cleansing liquid," evidence of its toxicity was mounting in the early- and mid-1930s (Thomas, 1934). Major producers as of 1934 included Carbide and Carbon Chemicals, Westvaco Chlorine, and Du Pont, who acquired the Roessler & Hasslacher Chemical Company and its Niagara Falls TCE facility in 1930 (United States Tariff Commission, 1934). Total United States production capacity as of the early 1930s

was estimated at 15 million pounds per year (Chem. Week, 1953). The use of TCE as a general anesthetic on humans was first reported in 1935 (Striker *et al.*, 1935).

1940–1960. By approximately 1940, TCE was reported to have replaced CTC as a solvent “to some extent,” due to its lack of corrosivity, ease of recovery and lower toxicity (Gabriel, 1941). TCE continued to be very widely accepted for metal degreasing, and it was reported to be rapidly replacing other solvents at this time (Byers, 1943). However, TCE’s use in dry-cleaning decreased significantly when it was found to attack certain cellulose acetate dyes (Chem. Week, 1953). The net effect of these trends was that TCE’s largest use in the 1940s became vapor degreasing of metals (Kirk and Othmer, 1949).

During World War II, TCE saw significantly increased use in degreasing metal machinery parts (Lowenheim and Moran, 1975). Supplies of TCE and other solvents were controlled so that military demands could be met. Manufacturers of TCE during the war years included Dow, Du Pont and Westvaco Chlorine (United States Tariff Commission, 1941–1945).

In contrast to the aftermath of World War I, the post-WW II years saw continued growth in chemical demand, promoting the further expansion of production capacity. In 1947, Hooker-Detrex began TCE production in Tacoma, Washington to satisfy West Coast demand. To supply the eastern United States market, the company completed construction of a new TCE production facility in Ashtabula, Ohio in mid-1950, with a capacity of 40 million pounds per year (Chem. Ind., 1949a; C&EN, 1950a). Niagara Alkali Company was completing construction of a new TCE production plant in Niagara Falls, New York as of 1949 (Chem. Ind., 1949b).

Despite the increased production capacity, supplies of TCE remained scarce in the late 1940s and early 1950s. Several TCE plants operated far below capacity due to shortages of chlorine. Makers of degreasing equipment offered to help users increase equipment efficiency as a means of decreasing TCE consumption, and offered to reclaim any used TCE shipped back to them by customers (C&EN, 1951a, 1951b). However, by the late 1950s, economic slowdown and increased imports shifted the TCE supply/demand balance toward oversupply. As of 1960, domestic PCE plants were operating at about 70% of capacity, and imports reached 60 million pounds (Chem. Eng., 1961).

In a recurrence of the cattle poisonings of the early 1920s, hemorrhagic diseases in cattle in the early 1950s were traced to animal feed containing TCE-extracted soybean meal. This finding caused most United States manufacturers to voluntarily withdraw soybean oil meals defatted with TCE in 1952 (Chem. Week., 1953; Huff, 1971).

In 1954, neutral inhibitor systems (described above) were developed to provide improved stabilization of TCE, helping to retain TCE’s hold on the degreasing market (Lowenheim and Moran, 1975). In 1958, Dow added a neutral grade of TCE to its product line (C&EN, 1958).

As of 1952, about 92% of TCE was consumed in vapor degreasing. The remainder was used in dry-

cleaning, fat and oil extraction, other cleaning applications, and as a heat exchange fluid (Chem. Week, 1953). The 1958 usage of TCE as an analgesic and anesthetic was estimated at 112 000 pounds (Huff, 1971). As of 1959–1960, the major producer of TCE was Du Pont, whose Niagara Falls facility accounted for about half the total United States production capacity of 485 million pounds. Other producers included Dow (70 million pound annual capacity); Hooker Chemical (70 million pounds); Detrex Chemical Industries, formerly Hooker-Detrex (75 million pounds); and the Columbia-Southern division of Pittsburgh Plate Glass (45 million pounds) (United States Tariff Commission, 1959; C&EN, 1960a; Chem. Eng., 1961).

1960–1970. During the 1960s, TCE’s combination of price and performance made it the most popular vapor degreasing solvent in the United States. This led to efforts to expand domestic production capacity and increase imports, primarily from Great Britain and Italy (C&EN, 1964a). In 1963, Pittsburgh Plate Glass announced plans to build a new PCE/TCE production facility in Lake Charles, Louisiana (C&EN, 1963). Hooker Chemical was adding TCE production capacity in Taft, Louisiana as of 1966 (C&EN, 1966a). After three years of marketing TCE produced by others, the Ethyl Corporation began production in Baton Rouge, Louisiana in 1967 and expanded the facility three years later (C&EN, 1967a, 1970a). Also in 1967, Diamond Alkali announced plans to build a TCE plant in Deer Park, Texas, with an approximate capacity of 50 million pounds (C&EN, 1967b, 1967c). Despite the increased production, TCE was again in short supply as of 1966 due to increased military demand associated with the Vietnam War, and reduction in imports caused by increased demand in Europe (C&EN, 1966a).

For TCE, the era of environmental regulation began early. In November 1965, the Los Angeles County Air Pollution Control District (APCD) proposed Rule 66, a regulation to limit solvent emissions from industrial facilities. The proposed rule, the first of its kind in the country, included a list of solvents to be regulated based on their role in promoting smog formation. The proposal provoked a storm of controversy, with industry representatives claiming that the rule would be impractical and costly. The controversy was resolved in what was generally viewed to be a model cooperative effort between regulators and industry. The APCD, the Chemical Manufacturers Association, and industry representatives collaborated to review existing data and the results of additional tests conducted on selected chemicals. The resulting modified rule was enacted into law without dissent in August 1966 (C&EN, 1966b, 1966c, 1966d).

Rule 66 exempted all chlorinated solvents except TCE. Implementation of Rule 66 therefore caused many users of TCE in Los Angeles County, such as the aerospace industry, to switch to PCE or TCA (C&EN, 1966b). TCE consumption in Los Angeles County, estimated at 40 million pounds per year, plummeted after the adoption of the rule (C&EN, 1969a). Effective dates ranged from July 1, 1967, for sources emitting greater than 500 pounds per day to March 1, 1968, for

sources emitting between 15 and 100 pounds per day (C&EN, 1966d).

1970–1980. The use of TCE in the United States peaked in 1970, and thereafter began a significant decline due to a combination of several regulatory and economic factors. The 1970 Clean Air Act (CAA) controlled TCE as a VOC due to its suspected contribution to ozone and smog formation. As a result, limitations on TCE emissions were placed on users in ozone nonattainment areas. TCE use was also negatively affected by the National Cancer Institute's (NCI) March 1975 finding that TCE caused cancerous tumor growths in mice livers (NCI, 1976). This finding probably influenced the EPA to include TCE on its Hazardous Substance List in 1976. As a result of NCI's finding, the General Foods Corporation announced in July 1975 that it would cease the use of TCE in the decaffeination of its Sanka[®] and Brim[®] brands, and would begin using methylene chloride as a substitute (C&EN, 1975a). Outright bans on TCE in states such as Rhode Island affected consumption, and led some manufacturers to promote the use of PCE and TCA as alternative solvents (Chem. Mktg. Rep., 1975). In late 1977, the Food and Drug Administration (FDA) banned the direct or indirect use of TCE in food, bringing an end to TCE's uses in hop extraction, coffee decaffeination, and spice oleoresin isolation (Kroschwitz and Howe-Grant, 1991).

In 1971, PPG Industries announced plans to triple the capacity of its Louisiana PCE/TCE production facility (C&EN, 1971). Between 1971 and 1978, the rising cost of acetylene caused a series of shutdowns of TCE plants using the acetylene production process. The shutdown of Du Pont's Niagara Falls facility, discussed in part 1 of this paper, became effective in 1972. As part of Du Pont's 1970 agreement related to the closing of the Niagara Falls plant, Diamond Shamrock adopted Du Pont's "Triclene" trade name for TCE (C&EN, 1970b). Hooker Chemical shut down the last acetylene-based PCE/TCE plant in 1978. The plant shutdowns led to shortages and a doubling in price between 1972 and 1976. Despite the increased prices, chemical manufacturers were reluctant to provide new capacity because of TCE's uncertain future under existing and proposed pollution control regulations (Lowenheim and Moran, 1975). The price of TCE also doubled between 1975 and 1985 (Kroschwitz and Howe-Grant, 1991). These factors combined to lead to the popularity of TCA as a TCE substitute.

Major producers of TCE as of 1974 included Dow Chemical, Ethyl Corporation, Occidental Petroleum (successor of Hooker Chemical), PPG Industries, and Diamond Shamrock (USDHHS, 1975; Kroschwitz and Howe-Grant, 1991). Together, Dow and PPG provided approximately 70% of total output (Seltzer, 1975). In the early 1970s, approximately 87% of TCE produced in the United States was used in vapor degreasing, 3% as an extraction solvent, and 8% was exported (Lowenheim and Moran, 1975). By about 1974, the percentage used in degreasing had dropped to 80%. Due largely to the growth in TCA usage, TCE's share of the vapor degreasing market dropped from 82 to 42% between 1970 and 1976 (Grayson and Eckroth, 1979).

1980–1990. The 1980s saw tightening environmental regulations and an average decline of 6% per year in TCE production (USDHHS, 1975). Beginning in 1980, TCE wastes were regulated as hazardous waste, as spent solvents (F001/F002) and as discarded commercial products (U228). Under the Safe Drinking Water Act (SDWA), a Maximum Contaminant Level (MCL) was proposed for TCE in November 1985, finalized in July 1987 and became effective January 1989 (Pontius, 1990). In 1989, the Occupational Safety and Health Administration lowered its Permissible Exposure Limit (PEL) from 100 to 50 parts per million, further increasing pressure on employers to seek alternative solvents (Kroschwitz and Howe-Grant, 1991).

Several manufacturers ceased TCE production in the 1980s, including Occidental Petroleum in 1980 and Ethyl Corporation in October 1982. By February 1983, only Dow and PPG Industries remained as TCE producers. TCE's use in the automotive and metal industries decreased in the early 1980s due to economic recession, resulting in excess supply in the market (Chem. Mktg. Rep., 1983). Significant new uses for TCE did not materialize in the 1980s. Between 1980 and 1985, strength of the United States dollar helped TCE imports rise from 8 to 40 million pounds, while exports decreased from 60 to 18 million pounds. As of 1985, it was estimated that 80% of TCE was used in cleaning and degreasing, 5% in chemical production, 5% in other uses and 10% was exported (Chem. Mktg. Rep., 1986).

1990–2000. During the 1990s, TCE use increased as it became a suggested replacement for other solvents banned under the 1990 CAA amendments, such as TCA and CFC-113. TCE also saw increased use as a feedstock for chlorofluorocarbon (CFC) replacements such as HFC-134a. The increase in TCE use is demonstrated in part by Dow Chemical's 1994 conversion of its 220 million pound per year TCA plant in Stade, Germany to TCE production (Kirschner, 1994). Although production data are not available from the United States International Trade Commission, United States consumption of TCE reportedly rose approximately 10% per year between 1993 and 1996 (Leder, 1999).

As of approximately 1991, TCE's use in metal cleaning and degreasing was estimated at 90% of production (Chem. Mktg. Rep., 1992). By 1995, this figure had decreased to about 55%, with 41% being used as a chemical intermediate (HSIA, 1996). As of 1998, TCE's largest end use was as a replacement solvent for TCA (Leder, 1999). As of 1997, Dow was expanding TCE production at its Freeport, Texas facility. Dow and PPG remained the only United States producers (Chem. Mktg. Rep., 1997).

1,1,1-Trichloroethane (TCA)

TCA, also known by the chemical and trade names listed in Table 3, became a widely used replacement for CTC, TCE and PCE in metal degreasing and cleaning applications. The appeal of TCA was that it offered excellent solvency for greases, oils, tars, waxes and many other organic materials, but was significantly less toxic than the chemicals it replaced. A chemical industry spokesman called TCA "by far the most

Table 3. Synonyms for 1,1,1-trichloroethane

Chemical names	
alpha-trichloroethane	
alpha-trichloromethane	
MCF	
methyl chloroform	
methyltrichloromethane	
trichloromethylmethane	
Trade names	
Axothene No. 3	
Barcothane Nu	
Blakeothane	
Blakesolv 421	
CF2 Film Clean	
Chlorothene VG (<i>Dow Chemical</i>)*	
Chlorothene NU (<i>Dow Chemical</i>)	
Chlorothene (<i>Dow Chemical</i>)	
Cloromane	
Dowelene WR (<i>Dow Chemical</i>)	
Dyno-Sol	
ECCO 1550	
Ethyl 111 Trichloethane (MPG)	
Insolv NU	
Insolv VG	
Kold Phil	
Kwik-Solv	
Lectrasolv 170	
Methyl Chloroform Tech	
Nacon 425	
NCI-C04626	
One, One, One	
Penolene 643	
Perm-Ethane DG (<i>Permathene</i>)	
Saf-T-Chlor	
Solvent M-50	
Solvent 111 (<i>Vulcan Materials</i>)	
Sumco 33	
Tri-Ethane (<i>PPG Industries</i>)	
Tri-Ethane Type 314 (<i>PPG Industries</i>)	
Tri-Ethane Type 315 (<i>PPG Industries</i>)	
Tri-Ethane Type 324 (<i>PPG Industries</i>)	
Tri-Ethane Type 329 (<i>PPG Industries</i>)	
Triple One	
V-303	
Vatron 111	

*Manufacturer name in italics.

Table 4. Major manufacturers of 1,1,1-trichloroethane

Company	Approximate period of manufacture
Dow Chemical	1936–1994
Ethyl Corporation	1964–1976
PPG Industries	1962–present
Vulcan Materials	1970–present

Sources include United States Tariff Commission, 1921–1972; USITC, 1973–1994; and company Web sites.

used, easiest, and efficient cleaning solvent” (Kirschner, 1994). A list of TCA manufacturers and their approximate periods of production is shown in Table 4. TCA production data are shown in Figure 2.

Uses

TCA's primary end uses were cold-cleaning, vapor degreasing and ultrasonic cleaning of metal parts for the removal of greases, oils and waxes. As a degreasing solvent, TCA was used by the aircraft, automotive, electronic and missile industries, among others. Among the many items cleaned using TCA were printing presses, precision instruments, food packaging, machinery, missile hardware, paint masks, photographic film, printed circuit boards, semiconductors, plastic molds, motors, generators, and appliances. TCA was used in spray and solid pesticides, solid rodenticides, drain cleaners, and carpet glue. Many brands of fire ant insecticides were composed almost entirely of TCA (EDF, 2000). In dry-cleaning, TCA was used to clean leather and suede garments. It was also used in the production of aerosols, adhesives, coatings, fluoropolymers, inks, textiles, and electronics. Minor applications included use as a mold-release carrier, a wig cleaner, an asphalt extracting agent for paving aggregate, a component of shoe polish, a lubricant in cutting oils and a solvent in the application of water and oil repellent to paper and textiles. The use of TCA as a feedstock for hydrochlorofluorocarbons (HCFCs) became important as a result of the phase-out of CFCs (Lowenheim and Moran, 1975; USDHHS, 1975;

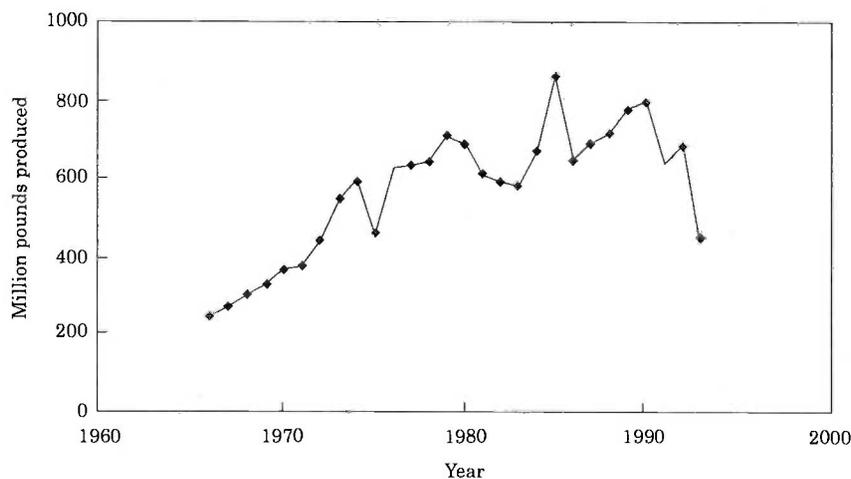


Figure 2. United States production of 1,1,1-trichloroethane (TCA).

Aviado *et al.*, 1976; Kroschwitz and Howe-Grant, 1991; HSIA, 1994; USEPA, 1994).

TCA was used in aerosol products, both as a solvent and as a low-pressure propellant. Aerosol products containing TCA included hair sprays, cosmetics, oven cleaners, spot removers, furniture polishes, automotive lubricants, automotive choke cleaners, water repellents, adhesives (Aviado, 1976) and guitar string lubricants.

Production methods

In 1931, a process for making TCA through the chlorination of 1,1-dichloroethane was published (Sutton, 1931). That same year, a German patent was issued for TCA production by hydrochlorination, involving the addition of hydrochloric acid to 1,1-dichloroethylene in the presence of a FeCl_3 catalyst (Farbenindustrie, 1931). These two basic processes remained the major production methods throughout TCA's period of use, with the chlorination method (using various feedstocks) being predominant (Lowenheim and Moran, 1975; McKetta and Cunningham, 1979). A United States patent for modifications to the 1,1-dichloroethylene chlorination process was issued to Dow Chemical in 1940 (Nutting and Huscher, 1940). Dow, Vulcan and PPG Industries used the hydrochlorination method (SRI International, 1985).

TCA was also produced by the noncatalytic chlorination of ethane, a process that was patented by the Vulcan Materials Company in 1963 (Vulcan, 1963). This process also yields various other chlorinated ethanes and ethenes. Vulcan used this process at one of their Geismar, Louisiana facilities until its shutdown in 1979 (Gerhartz, 1986).

Unstabilized TCA can react vigorously with aluminum, forming corrosive by-products. As discussed below, the difficulty in finding a suitable stabilization agent for TCA considerably slowed its acceptance throughout the vapor degreasing market, and in particular in the aerospace industry. After suitable stabilizers were incorporated, TCA found wide use in cold-cleaning and vapor degreasing of all common metals, including aluminum. The inhibitors typically included an acid acceptor and a metal stabilizer, with the formulation varying not only between manufacturers, but also between product grades produced by the same manufacturer.

Because the reaction between aluminum and unstabilized TCA can be vigorous, stabilizer concentrations in commercial grades of TCA were higher than those in most other chlorinated solvents. Vapor degreasing grades of TCA contained from 3 to 8% stabilizers and additives. Chemicals used included 1,4-dioxane, 1,3-dioxolane, 1,2-butyleneoxide, N-methylpyrrole, methylethylketone, ethyl acetate, acrylonitrile, nitromethane, dialkyl sulfoxides, sulfides and sulfites, tetraethyllead, *tert*- and *sec*-butylalcohol, isopropyl alcohol, morpholine, tetrahydrofuran, and toluene (Standen, 1964; McKetta and Cunningham, 1979; Archer, 1984; Kroschwitz and Howe-Grant, 1991).

History of use

TCA was first prepared by Regnault in about 1840 (Kroschwitz and Howe-Grant, 1991), but did not see

widespread commercial use until the middle of the 20th century. TCA was being manufactured earlier in the 20th century, but often as an unwanted byproduct in chlorinated hydrocarbon processes (Gerhartz, 1986). A 1914 review of rubber solvents included TCA in a list of chlorinated compounds being manufactured in Europe (India Rubber World, 1914).

TCA first appeared in the Census of Dyes and Synthetic Organic Chemicals in 1924, but did not reappear until 1936 (United States Tariff Commission, 1924–1936). Furthermore TCA is not included in an exhaustive review of chemicals and their uses published in 1939 (Gregory, 1939). These and other sources discussed below strongly indicate that TCA did not see appreciable commercial use as an end product until the 1950s.

In 1932, a patent application was made for the use of TCA and other chlorinated ethanes as dry-cleaning fluids (Parkhurst, 1934). The patent, issued in 1934, covered the use of TCA in dry-cleaning, either alone or as an ingredient of a mixture. However, no information was found to suggest that TCA was used in dry-cleaning prior to the 1950s.

1940–1950. A 1941 review of new solvents did not mention TCA, suggesting that it was not widely used at this time (Gabriel, 1941). TCA was not included on 1940s market price lists, which typically listed chemicals used in large commercial quantities (Ind. Eng. Chem., 1940; C&EN, 1948–1949). The 1949 edition of Kirk and Othmer's *Encyclopedia of Chemical Technology* (Kirk and Othmer, 1949) stated that "although 1,1,1-trichloroethane is not commercially important, some of its derivatives are effective insecticides". Chief among these insecticide derivatives was DDT.

1950–1960. TCA made a brief appearance on market price lists in July 1950 (C&EN, 1950b), but did not return until April 1951 (C&EN, 1951c). Dow Chemical introduced the first large-quantity commercial brand of TCA, Chlorothene, in 1954 (Chem. Eng., 1961; C&EN, 1962). The Chlorothene name was trademarked in September 1954, with a date of first commercial use listed as August 25, 1954 (USPTO, 2000). The Chlorothene line was to become probably the most widely used brand of TCA in the United States. Dow Chemical remained the sole United States producer of TCA until 1962.

TCA's first commercial application was as a cold-cleaning solvent, where it served as a replacement for CTC (Barber, 1957). Its early use was limited to cold-cleaning applications because TCA tended to break down and corrode certain metals (particularly aluminum) under the higher temperatures used in vapor degreasing (Lowenheim and Moran, 1975).

TCA's other early use was as an aerosol propellant in products such as insecticides and hair sprays. Dow promoted the use of Chlorothene in aerosol formulations in late 1956 and early 1957 (Chem. Week, 1956; Barber, 1957). However, to prevent corrosion, Chlorothene was not recommended for use in aluminum or zinc containers where water was present. In mid-1957, Dow publicized the results of toxicological studies showing that up to 26% Chlorothene could safely be used in hair sprays (Schober, 1958).

Prior to approximately 1957, TCA was not widely used because adequate stabilizer formulations could not be found. Stabilizers used for other chlorohydrocarbons were found to be largely ineffective with TCA. In 1954, a patent application was filed for the use of 1,4-dioxane as a TCA stabilizer. The addition of about 4% 1,4-dioxane allowed TCA to be used with aluminum, zinc and iron. A non-primary alkanol was also added to TCA to allow storage in steel drums without product discoloration (Bachtel, 1957). The improvement of this stabilizer formulation to allow the use of TCA in vapor degreasing was the subject of a 1955 patent application (Bachtel, 1958). These stabilizer formulations, along with over one hundred others specifically developed for TCA, would open up new markets (McKetta and Cunningham, 1979).

By late 1957, TCA was said to have gained widespread acceptance as a replacement for CTC, primarily in cold-cleaning applications (C&EN, 1957). Although TCA production figures for the 1950s are not available, Dow's capacity was limited to 20 million pounds per year until approximately 1961 (Chem. Eng., 1961).

1960–1970. Dow Chemical introduced Chlorothene NU in May 1960 (C&EN, 1960b). This widely used formulation, initially advertised for cold-cleaning use and subsequent recovery via distillation, used 1,4-dioxane as a stabilizing agent. In 1962, Dow added Dowclene EC to its product line. This TCA formulation featured a longer evaporation time than Chlorothene NU or TCE, and was specifically formulated for spray cleaning of large railroad equipment (C&EN, 1962). In 1965, Dow expanded its TCA line by introducing Dowclene WR, developed for cleaning microcircuitry and machined parts in the aerospace industry (C&EN, 1965). In 1967, a TCA/methylene chloride propellant mixture for use in aerosol products was introduced under the trade name Aerothene (Aviardo *et al.*, 1976).

Sources indicate that the use of TCA was still confined to cold-cleaning applications at the start of the 1960s. The second edition of the Kirk–Othmer encyclopedia, containing a summary of TCA information prepared in approximately 1961, states that “So far, probably because of lack of suitable stabilizers under the conditions of operation, [TCA] has not been employed for metal degreasing at elevated temperatures” (Standen, 1964). A 1961 article attributes TCA's sales growth to replacement of CTC in cold-cleaning applications (Chem. Eng., 1961).

Dow doubled its annual TCA production capacity to 40 million pounds in 1961. In 1962, PPG Industries became the second United States producer of TCA. PPG went on to expand its Lake Charles, Louisiana plant three times in the 1960s, increasing TCA capacity from 15 million to 175 million pounds per year (C&EN, 1970c). The Ethyl Corporation (headquartered in Richmond, Virginia after its 1962 acquisition by the Abermarle Paper Company) began TCA production in 1964 in Baton Rouge, Louisiana. Despite the growth in production capacity, TCA was reported as being in short supply in 1966 because of increased military use due to the Vietnam War (C&EN, 1966a).

In 1968, Vulcan Materials announced the construction of a TCA production facility in Geismar, Louisiana (C&EN, 1968). The facility began

production in 1970, making Vulcan the fourth significant TCA supplier. Diamond Alkali announced that TCA was being added to its product line in 1964 (C&EN, 1964b); however, the company was not reported as a TCA manufacturer in the annual Census of Synthetic Organic Chemicals until 1973 (USITC, 1973). By that time, the company was known as Diamond Shamrock, due to its January 1, 1968, merger with Shamrock Oil & Gas.

1970–1980. The 1970 CAA, as discussed previously, increased demand for TCA at the expense of TCE, PCE and methylene chloride. TCA was officially listed as exempt from the CAA Volatile Organic Compound regulations in July 1977 (USEPA, 1977). The use of TCA also increased due to shortages and rising prices of TCE in the early 1970s (Kroschwitz and Howe-Grant, 1991). The net result of these factors was that TCA production surpassed that of TCE in 1973 (United States Tariff Commission, 1972).

In 1970, Dow Chemical was in the process of building a new TCA plant in Freeport, Texas. The plant employed a new production process, and, upon completion, Dow was to convert its existing TCA facilities in Freeport to produce other chlorinated hydrocarbons (C&EN, 1969b). In 1975, PPG Industries announced the construction of a 300 million pound TCA production facility in Lake Charles, Louisiana, scheduled for completion in 1978 (C&EN, 1975b). Dow Chemical completed a 300 million pound TCA plant in Plaquemine, Louisiana in 1978, but left the plant idle because existing United States capacity was already about 300 million pounds greater than the annual demand (Chem. Mktg. Rep., 1979).

Problems with TCA use began to surface in the mid-to-late 1970s. In 1973, 21 deaths resulted from the reported abuse of aerosol decongestants containing TCA. This caused the Federal Drug Administration to recall the decongestants, and require the registration of all drugs containing TCA intended for human use (USFDA, 1973). In 1978, aerosol propellants were banned in an early effort to protect the stratospheric ozone layer. It was estimated that 6% of TCA produced in the United States was used in aerosols at the time. The use of TCA in septic system and cesspool cleaners came under attack in New York State in 1979. The detection of TCA and methylene chloride in dozens of Long Island municipal wells was attributed to the use of the cleaning chemicals. New York State requested that 10 manufacturers cease marketing of the cleaners (Chem. Week, 1979).

Many industry insiders did not expect these problems to have a serious effect on the TCA market (Lowenheim and Moran, 1975). However, in 1976, Ethyl Corporation exited the TCA business, and in early 1979, Vulcan Chemicals shut down a 70 million pound per year ethane-based production facility in Geismar, Louisiana (SRI International, 1985). As of 1975, 33% of TCA produced in the United States was used in cold-cleaning, 29.6% in vapor degreasing, 20.5% in the manufacture of copolymers, 11.8% was exported, and 5.1% was used for miscellaneous purposes (Khan and Hughes, 1979).

1980–1990. Under the 1980 Resource Conservation and Recovery Act regulations, TCA was classified as hazardous when present in spent solvents (F001 and F002) and as a discarded commercial product (U226). Under the Safe Drinking Water Act, an MCL of 200 micrograms per liter of TCA was proposed in November 1985, finalized in July 1987, and became effective in January 1989 (Pontius, 1990).

As of 1984, vapor degreasing and cold-cleaning were estimated to consume approximately 65% of the total TCA produced. By the late 1980s, this figure dropped to 50% (Kroschwitz and Howe-Grant, 1991). A chemical encyclopedia published in 1986 reported that new applications for TCA were being found in textile processing and dry-cleaning, and cited TCA as a potential replacement for the widely used PCE (Gerhartz, 1986). However, production capacity continued to far exceed demand. Dow's Plaquemine facility remained idle, and PPG Industries placed a 175 million pound unit in Lake Charles, Louisiana on standby (Chem. Mktg. Rep., 1982). During the 1980s, Dow remained the leading TCA manufacturer, followed by Vulcan Chemicals (Geismar, Louisiana) and PPG Industries (Lake Charles).

1990–2000. The 1990s saw the future of TCA as a solvent come to an end. Market conditions for TCA rapidly changed in response to regulatory pressure and shifting demand. Beginning on January 1, 1991, TCA became subject to a Federal excise tax due to its ozone-depleting potential. On May 15, 1993, CAA labeling requirements went into effect mandating that most TCA-containing products carry a warning to identify the presence of an ozone-depleting substance. Between 1992 and 1993, TCA list prices increased from 40 to 64.5 cents per pound. Federal excise taxes, not included in list prices, increased from 14 cents per pound in 1992, to 21.1 cents in 1993, 43.5 cents in 1994, and 53.5 cents in 1995 (Chem. Mktg. Rep., 1993; HSA, 1994). TCA use in the United States continued to decrease between 1993 and 1996, and prices in 1997 were 10 times higher than in 1994 (Leder, 1999).

Under the Toxics Release Inventory "33–50" program, EPA called for voluntary reduction of emission of TCA and 16 other chemicals. Target reductions were 33% by 1992, and 50% by 1995, relative to 1988 usage rates (Kirschner, 1994). These reductions were accelerated and made mandatory under the CAA amendments.

The 1990 CAA amendments classified TCA as a Hazardous Air Pollutant under Section 112, and, more significantly, regulated TCA as an ozone-depleting chemical under Title VI. The amendments included a complete phase-out of "emissive" TCA uses by December 31, 1995. Although TCA was believed to have only 15% of the ozone-depleting potential of CFC-12, large quantities were being used in emissive applications such as metal cleaning and degreasing (Kroschwitz and Howe-Grant, 1991). Interim deadlines adopted as of December 30, 1993, called for a 50% cut in TCA usage by January 1, 1994, and a 70% decrease in 1995, relative to 1989 levels (USEPA, 1993). The terms of the phase-out allowed use after the December 1995 deadline to deplete existing inventories, and allowed United States producers to sell TCA for

emissive use in developing countries. TCA could still be used after 1996 as an intermediate product, for example as a feedstock for production of other chemicals. This represented somewhat of a reprieve for TCA, because many potential CFC replacements used TCA as a feedstock. However, under the terms of the amended Montreal Protocol, TCA is to be completely phased out as of 2002. Exceptions exist for essential uses such as fatigue and corrosion testing of airplane engines and parts (Randle and Bosco, 1991).

In anticipation of the impending phase-out, the leading United States producer of TCA, Dow Chemical, ceased TCA production by shutting down its 500 million pound per year production facility in Freeport, Texas in February 1994 (Kirschner 1994). PPG Industries and Vulcan Chemicals did not shut down plants at this time, but, as required, cut back production in 1995 to 30% of their 1989 levels. PPG Industries had 350 million pounds capacity at its Lake Charles, Louisiana plant, and Vulcan Materials Company had 200 million pounds capacity in Geismar, Louisiana (Chem. Eng., 1995). As of 1994, 60% of TCA was used as a chemical intermediate, 25% in cold-cleaning and degreasing, 5% in adhesives, and 10% in miscellaneous uses (Chem. Mktg. Rep., 1995).

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Metal Cleaning

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SAMUEL SPRING

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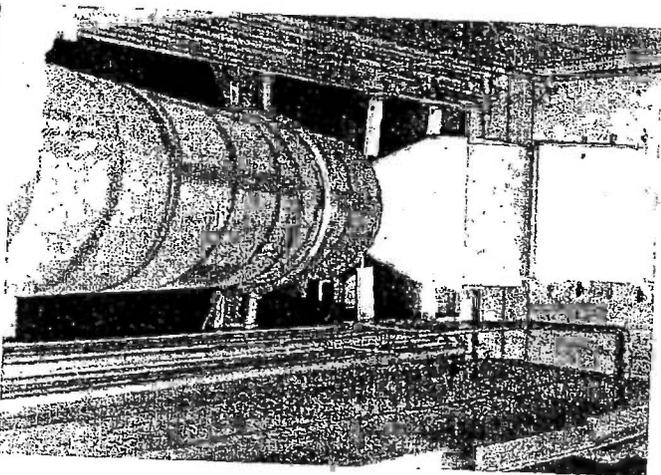


Figure 14. Screw conveyor drum. (Courtesy Metal Wash Machinery Corp., Elizabeth, N.J.)

are subjected to pressure spraying. In such installations, the restrictions and advantages of spray cleaning determine the conditions for operation.

Cleaning by Circulation

This is used mainly in plant or equipment maintenance. In large diameter pipes, the action is largely one of exposing fresh cleaner to the surface rather than a high level of agitation. In smaller pipes, there may be considerable agitation dependent on the rate of flow of the solution and the hydraulic properties of the pipe, i.e., pressure, smoothness, and configuration.

In most cases the cleaner is returned to a holding tank or sump where it can be heated to compensate for the temperature drop during circulation. The surge in the holding tank upon return of the cleaning solution may generate large quantities of foam. Foam generation during circulation is minimal. However, it is better to use high surfactant containing

cleaners which do foam on return to the holding tank and to break the foam with a foam suppressant (see Chapter 5) than to compromise on less efficient but lower foaming detergents. A special case involves the cleaning of heat exchangers. Here the heat can be supplied through the equipment which makes matters more convenient but sometimes results in excessive temperatures which may cause throw-down from some cleaners. This can be pre-investigated by laboratory test in a closed system, e.g., a capped pipe, where high temperatures can be generated to simulate the production operation.

Another special case which falls between spray cleaning and circulation cleaning has to do with cleaning the interior of storage tanks, tank cars or trucks, and large vessels. The cleaner may be circulated by flooding the walls of the vessel or it may be sprayed in some practical fashion. A specific type of installation is schematized in Figure 15. Here a special spray head is employed which rotates under the pressure of liquid being pumped and throws the cleaner against the walls of the vessel. The cleaner flows back to the holding tank and is screened and heated if necessary before being pumped out again.

Vapor Degreasing

In vapor degreasing the part is introduced into a chamber saturated with the vapors of a chlorinated hydrocarbon distilled from a vat of the boiling solvent (Figure 16). Since the metal part is cooler than the vapors, the latter condense over the part and flush away the soil as the condensed solvent drips down. Because of the nature of the distillation process, the vapors and condensate are composed of almost pure solvent; the work part is thereby rinsed with pure solvent. While it is intended that the part be left clean by this procedure, this is not always true as some soils are not soluble in the solvent and there is almost always a trace of oily residue remaining from the solvent. Chlorinated solvents* are admirably suited to the vapor degreasing process because they yield very dense vapors which minimize dissipation by air currents. The walls of the chamber are chilled by circulation of cool water to condense most of the fumes that leave the cleaning area. In spite of this, a certain amount of solvent gets into the atmosphere, requiring care in ventilation and increasing the cost of the operation. One almost always recognizes the presence of a vapor degreasing machine by the characteristic odor that permeates the area.

The solvent used in most vapor degreasers is trichloroethylene. There has been a trend toward the use of the higher boiling (127°C or 250°F)

* See properties listed in Chapter 2.

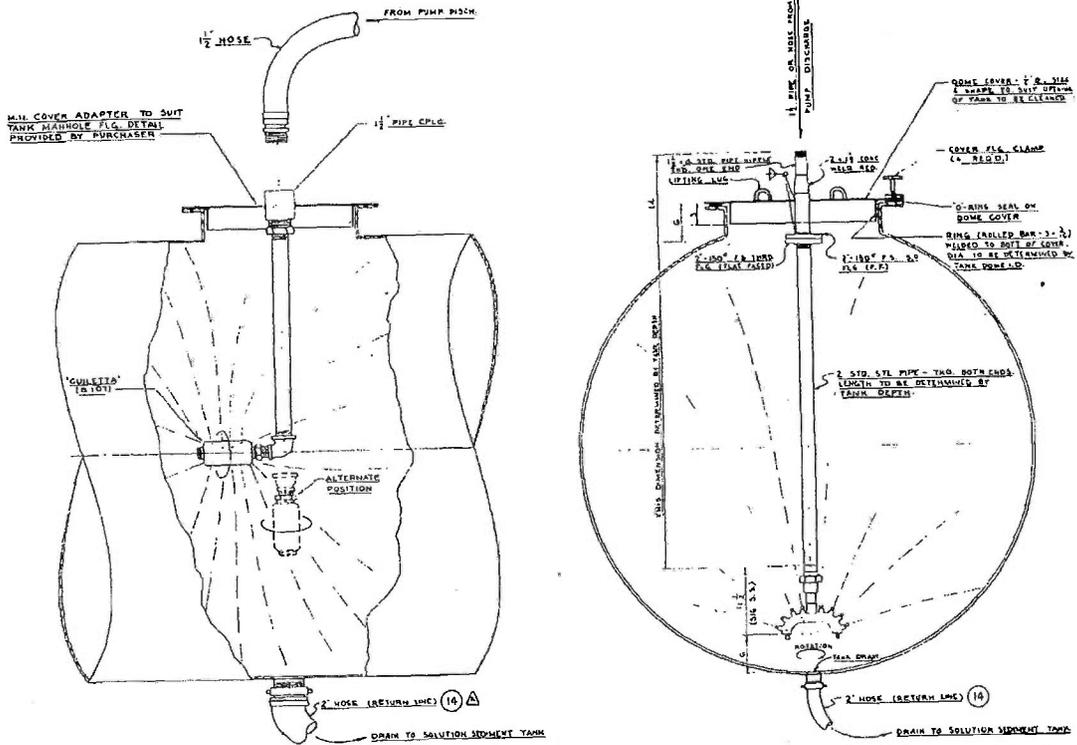


Figure 15. Schematic of tank cleaning unit. Pipe with rotating head is lowered into tank; collected effluent is re-circulated. (Courtesy Kelite Corp., Los Angeles)

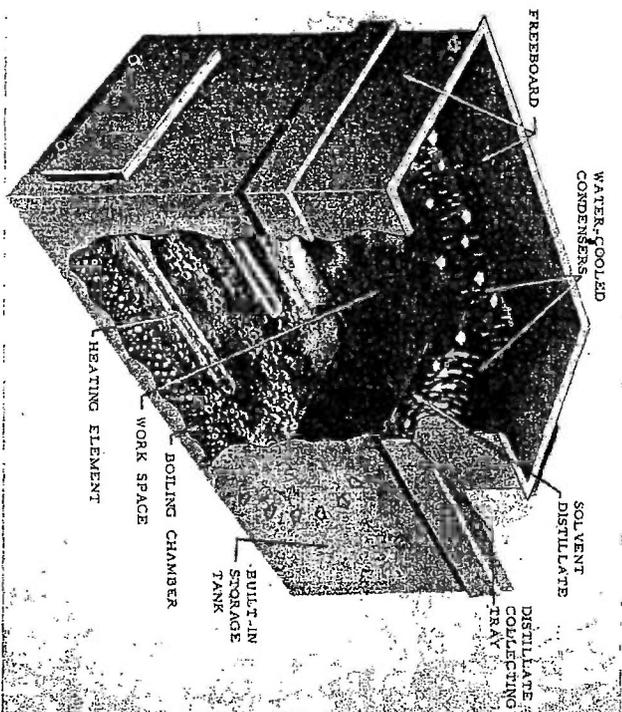


Figure 16. Basic vapor degreaser. Heater boils solvent, generally trichloroethylene or perchloroethylene, forming vapor zone. Solvent condenses on parts held in vapors; soil is dissolved, carried to sump. Water jacket sets maximum height of vapor zone; freeboard prevents vapor loss to outside air currents. (Courtesy Dettex Chem. Industries, Detroit)

perchloroethylene which is less volatile and therefore safer in that less accumulates in the air. The high temperature required to distill perchloroethylene is sometimes a hazard since personnel coming in contact with the parts or the machine may be burned.

The efficacy of the condensation process which yields fresh solvent is dependent on a number of factors including the temperature of the work, its specific heat, wall thickness, etc. The cooler the part and the faster the heat is removed, the better the condensation. Work should be arranged to avoid layers of which the lower layer condenses vapors and reaches temperature before the upper layer; should this occur, dripping from the upper layer would contaminate parts in the lower layer. Being the same temperature as the hot solvent, the lower layer could not further condense vapors to provide a flush with fresh solvent.

The above-mentioned condensation and flushing mechanism avoids a

TABLE 5. TYPICAL APPLICATIONS FOR VAPOR-DEGREASING SOLVENTS

Application	Solvent	Approximate	Factors Affecting Selection
		Vapor Temperature, °F	
Removal of soils from parts	Trichloroethylene	188	Most commonly used degreasing solvent
Removal of slightly soluble (high melting) soils	Perchloroethylene	250	Used where higher operating temperature is desirable
Removal of water films from metals	Perchloroethylene	250	Rapid and complete drying in one operation
Cleaning coils and components for electric motors	Methyl chloroform	165	Solvent must not damage wire coating or sealing agents. Requires special equipment design. Selection should be based on preliminary trials
	Trichlorotrifluoroethane	118	
Cleaning temperature-sensitive materials	Methylene chloride	104	Used where parts must not be exposed to higher vapor temperatures during cleaning. Special corrosion resistant equipment is required
	Trichlorotrifluoroethane	118	
Cleaning components for rockets or missiles	Trichloroethylene	188	Cleaned parts must be free of soils or residues which might react with oxidizers
	Trichloroethylene	188	For cleaning efficiency beyond that obtained from standard vapor degreasing. Solvent must be kept clean by continuous distillation and filtration during use. Selection should be based on preliminary trials
	Perchloroethylene	250	
	Methylene chloride	104	
	Fluorinated hydrocarbon	118	

major disadvantage of solvent cleaning since the continual rinsing with fresh solvent avoids a substantial residue after evaporation. Vapor degreasers work rapidly and efficiently to remove rust preventive oils, heavy mineral oils, viscous or polymerized oil-base cutting lubricants, waxes, and high molecular weight chlorinated oils used as lubricants; these soils are extremely difficult to remove otherwise. They should not be used for

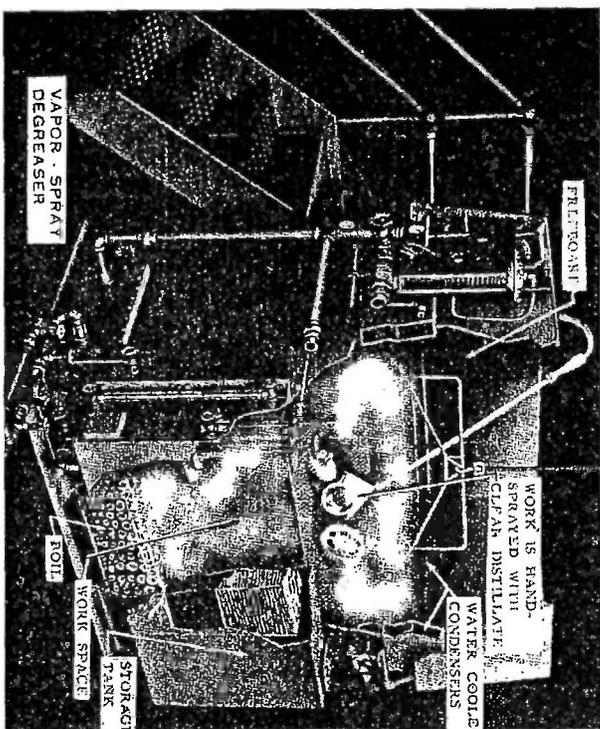
soaps, soluble oils, emulsion drawing compounds or other soils containing water; lubricating greases rich in soaps, etc. Vapor degreasing is used broadly as a pre-cleaner to remove buffing compounds made with high melting waxes, especially from aluminum or zinc base die castings that might be harmed by strong alkaline cleaner.

The condensation of vapor does not provide much agitation so that insoluble residues often are not removed with the solvent-soluble soils. This poses a greater problem than might be supposed in instances in which finely divided particulate soil is mixed with oily soil. The removal of the oily soil leaves the finely divided solids behind in such condition that they are strongly attracted to the metal. For example, if parts covered with a buffing compound, composed of finely divided abrasive particles (such as tripoli or rouge) in a waxy base, are treated in a single stage vapor degreaser, the wax is dissolved but the abrasive particles might remain behind. These particles can be wiped off the surface readily. However, removal with a detergent or hot alkaline cleaner may be quite unsuccessful unless vigorous agitation is employed. On the other hand, modest agitation may be adequate if supplied while the solvent is dissolving the waxy matter. Hence, a very popular machine contains a cold or warm solvent spray followed by a vapor condensing flush (Figure 17).

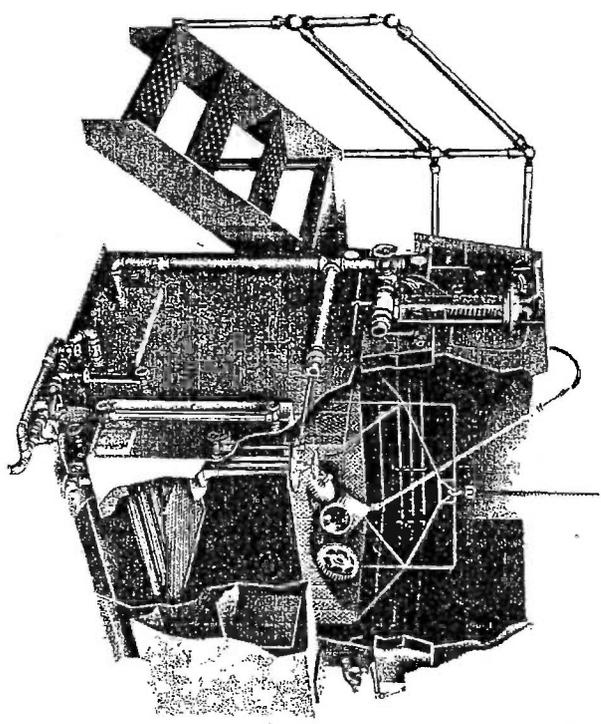
Parts of such shape that the vapor or spray cannot easily contact all surfaces, such as bulk quantities of small parts, tubing, etc. are treated in equipment which includes an immersion stage in warm solvent. The parts are drained and then go into a vapor stage. This is often carried out in an open top tank. The immersion solvent is kept below the boiling point so that some condensation takes place in the vapor stage. Sometimes immersion in boiling solvent is followed by immersion in cool solvent in order to ensure condensation in the next stage since the metal must be cooler than the vapor.

Another cycle first employs a vapor condensation stage to remove the bulk of the soil, a warm spray to take off stubborn residues, and a final condensation flush, which is less efficient than the first because of the warmth of the parts, but still effective (Figure 18). Combinations of such stages may also be used with an ultrasonic cleaning stage where cleaning must be absolutely complete.

The vapor degreaser, especially of the open tank type, should be located away from drafts which have the effect of blowing away solvent vapors before they can be condensed by cooling. The loss into the air is expensive and dangerous. At the same time, sufficient air circulation is necessary to prevent accumulation of toxic vapors. Adequate ventilation space is essential. For example, if the open surface at the tank is 600 sq in., the



(a)



(b)

Figure 17 (a) and (b). Vapor degreaser with manually operated solvent spray. (Courtesy Detrex Chem. Industries, Inc., Detroit)

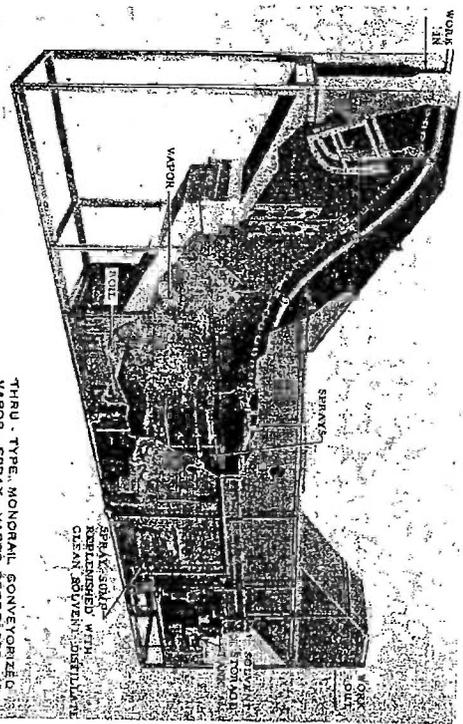


Figure 18. Vapor degreasing machine for removal of complex soils by vapor-spray-vapor treatment. (Courtesy Detrex Industries, Inc., Detroit)

equipment should be in a space of no less than 8000 cu ft. High pressure steam, 50 to 60 psi, is required for perchlorethylene but should be avoided with trichlorethylene to prevent overheating. The solvent layer must not be permitted to fall so much that the heating element is exposed since this promotes overheating and acid formation.

Water should be kept out of the degreaser to reduce hydrolysis. A water separator should be provided to remove excess water. If hydrolysis takes place, which might occur if aluminum and water are present or overheating occurs, the odor of hydrochloric acid may be noticed. Stabilizers are present in the solvent to neutralize hydrochloric acid or prevent hydrolysis. If excessive acid has been generated, the machine should be drained and washed out with an alkaline solution such as soda ash to neutralize the acid, and then thoroughly dried before recharging with fresh solvent or neutralized and distilled solvent. When using perchlorethylene, it is possible to drive off the water since it has a lower boiling point than the solvent. To do this, the cooling section of the vapor degreaser should not be too efficient or the water will condense as well as solvent. This may be regulated by reducing the flow of the cooling water. It is possible to separate the water from the trichlorethylene to some extent by less efficient cooling. In this case, the water condenses first and is drained off while the solvent condenses in an upper zone. In

most plants the cooling water of the vapor degreasing machine is directed to a rinse tank or other purpose rather than being discarded, unless it is chilled in a cooling tower and used again.

Oils accumulate in the chlorinated solvent with coincident increase in the boiling point. At a reasonable point, the solvent requires distillation and rejection of the oil. This point may be determined by measurement of the temperature of the boiling solvent or the specific gravity of the solution after cooling. Some illustrative data on boiling point are given in Chapter 11 on control of cleaning baths.

References

Other Topics

See References Chap. 1.

Vapor Degreasing

1. I. Mellan, "Industrial Solvents," Reinhold Publishing Corp., New York, 1956. (2nd edition).
2. T. S. Kearney and C. E. Kircher, *Metal Progress*, **77**, 87 (April 1960); **77**, 93 (May 1960).
3. H. Nulle, 200-210; M. Randall, 210-212, "Metal Finishing Guidebook," Metals and Plastics, Pub., Inc. Westwood, New Jersey, 1961.
4. C. E. Kircher, *ASTM Bulletin*, **219**, 44 (1957).

CHAPTER

4

Special Methods of Cleaning

These include electrocleaning, steam cleaning, abrasive cleaning, and cleaning with ultrasonic energy. Steam cleaning is a general method used more in maintenance than in production cleaning, even though metal cleaning is involved. It does have application to production cleaning, however, and has more potential in this direction than is generally recognized. The subject order of Chapter 3 is used since this chapter is a continuation of methods of cleaning.

Electrocleaning

The part to be cleaned is made an electrode in a solution which can carry current through its ions. Upon passage of direct current, water is electrolyzed into hydrogen gas at the cathode and oxygen gas at the anode. The generation of gas in large volumes provides a high level of agitation, especially at those areas where the soil is partially removed. Here current can pass readily to or from the metal. In addition, the electrical charge imposed on the work is important in removing certain complex soils.

In the preparation of metal for electroplating, an electrocleaning stage is almost always used (Figure 19). Electrocleaning can also be used where high quality metal cleaning is to be carried out even if the metal is not to be electroplated. This is seldom done because of the expense of putting in direct current generators or rectifiers, whereas this type of equipment is available in electroplating establishments.

The work may be made either the cathode or the anode. If it is made the cathode, twice as much gas is generated as when it is the anode. On this basis, so-called direct current (cathodic cleaning) was used to a great extent at one time. However, it now appears that reverse current (anodic cleaning) is more desirable for most applications because there are fewer detrimental side effects.

Chemical Safety Data Sheet SD-14

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

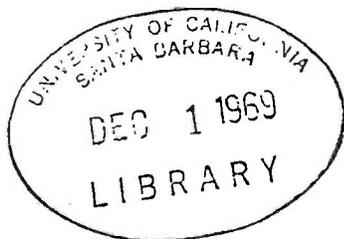
TRICHLOROETHYLENE

ADOPTED 1947

FIRST REVISION 1948

SECOND REVISION 1956

Chemicals in any form can be safely stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.



MCA

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Chemical Safety Data Sheet

TRICHLOROETHYLENE

PREFACE

Trichloroethylene may be harmful by inhalation, by prolonged or repeated contact with the skin or mucous membranes, or when taken by mouth.

The Interstate Commerce Commission does not classify it as a dangerous article requiring special packaging but the Manufacturing Chemists' Association recommends the use of a warning label on containers.

Suggestions for the safe handling of trichloroethylene are given in the body of the data sheet.

FIRST AID — SEE PAGE 15

Chemical Safety Data Sheet

TRICHLOROETHYLENE

Adopted 1947

Revised 1948

Revised 1956

1. NAMES

Chemical Name: Trichloroethylene
 Common Names: Trichlorethylene, Ethylene Trichloride
 Formula: $\text{CHCl}_2\text{CCl}_2$

2. PROPERTIES

2.1 GRADES

Technical or Dry Cleaning, Degreasing and Extraction

2.2 PROPERTIES AND CHARACTERISTICS

Physical State.....Liquid
 Explosive Limits.....Not flammable or explosive at ordinary room temperatures but moderately flammable at higher temperatures.
 Flash Point.....Practically nonflammable.
 Boiling Point (760 mm.).....87.0°C. (188°F.) Lange.
 Color.....Clear and colorless unless marked with an identifying dye, e.g., degreasing grade.
 Corrosivity.....Stabilized trichloroethylene may be used in the presence of air, water and light with any of the common construction metals at temperatures up to 120°C. (248°F.).
 Hygroscopic.....No.
 Ignition Temperature.....410°C. (770°F.).
 Light Sensitivity.....See "Corrosivity" above.
 Melting Point.....-73°C. (-99°F.) Lange.
 Odor.....Somewhat similar to odor of chloroform.
 Reactivity.....Not dangerously reactive except that strong alkalis, such as caustic soda, may react with trichloroethylene to form explosive mixtures (dichloroacetylene). Weaker alkalis, such as trisodium phosphate, may be used with safety.
 Solubility in Water.....0.1 grams per 100 ml.
 Specific Gravity at 20°/4°C.
 (68°/39°F.) (Water = 1).....1.464
 Vapor Density (Air = 1).....4.54

VAPOR PRESSURE OF TRICHLOROETHYLENE

Temperature		Vapor Pressure mm. Mercury
°C	°F	
0	32	19.9
10	50	35.7
20	68	57.8
30.5	87	93.7
40	104	146.8
50	122	212
60	140	305.7
86.9	188	760

Threshold Limit.

100 ppm or 520 Mg/M³.

3. HAZARDS

3.1 HEALTH HAZARDS (See 10.)

Trichloroethylene may be harmful by inhalation, by prolonged or repeated contact with the skin or mucous membranes, or when taken by mouth. However, if proper precautions are constantly observed, this compound can be handled with safety.

3.2 FIRE HAZARD

3.2.1 The fire hazard is very small, trichloroethylene being classified by the Underwriters' Laboratories as nonflammable at ordinary tem-

peratures, and only slightly flammable at higher temperatures.

The fire hazard is rated 3, as determined by the U.L. Standard for Classification, in which ethyl ether rates 100, ethyl alcohol 60-70, and paraffin oil 10-20. In practical applications, such as cleaning fluids and vapor degreasing, the formation of combustible mixtures is extremely unlikely.

3.2.2 At very high temperatures, such as occur in open flames, trichloroethylene may decompose to give hydrochloric acid and other toxic products.

4. ENGINEERING CONTROL OF HAZARDS

4.1 BUILDING DESIGN

Processes should not be located near open flames, open electric heaters or high temperature operations, since trichloroethylene vapor exposed to such high temperatures may be decomposed to toxic and corrosive substances (See 3.2.2).

4.2 EQUIPMENT DESIGN

Processes should be designed so that the operator is not exposed to direct contact with trichloroethylene or its vapor. The technical problems of designing equipment, providing adequate ventilation and formulating operational procedures which promise maximum security and economy, can be handled best by engineers and safety specialists. Manufacturers of trichloroethylene, and of the equipment in which it is to be used, are always prepared to help with these problems, and to assist in maintaining safe working conditions. In most States, authoritative advice and assistance may also be obtained from the industrial hygiene division of the State health department, or from the labor department.

4.2.1 System Types

Depending upon the application, trichloroethylene may be used in any one of the three systems described below:

4.2.1.1 For the vapor degreasing of metals, equipment manufacturers have designed special open type machines in which the solvent liquid and vapor are controlled by balanced heat

input and cooling capacity of condensing coils, which establish a "vapor ceiling." Such vapor degreasing units should always be installed in locations free from draft conditions.

4.2.1.2 Partially closed equipment has been designed for the use of trichloroethylene in the dry cleaning industry. Such equipment, however, exhausts the greater part of the solvent vapor to the outside atmosphere, thereby minimizing exposure of the worker. Proper design of the machine ensures against seepage of solvent liquid and vapor during the cleaning operation. Partially closed systems are likewise adapted to metal degreasing operations in some conveyerized vapor units.

4.2.1.3 Extraction equipment designed for trichloroethylene is an example of a closed system design.

4.3 VENTILATION

4.3.1 General ventilation should be adequate for processes conducted in closed or partially closed equipment, but mechanical exhaust ventilation, preferably of the downdraft type, may be provided for clean-out and other special operations. Open top vapor degreasers, however, should be provided with suitable baffles and otherwise protected from drafts to avoid entrainment of trichloroethylene vapors. Where equipment is located in pits or depressions, separate mechanical exhaust ventilation should be installed at the lowest level.

4.3.2 Intakes to exhaust ventilating systems should be as close as possible to the point where

the vapor escapes or to the source of contamination and designed to draw the vapor away from the operator but not across his face.

4.4 AIR ANALYSIS

4.4.1 The maximum allowable concentration (threshold limit) is 200 ppm. by volume in air for an eight hour working day.

4.4.2 When checking concentrations of trichloroethylene vapor in the atmosphere, care is required to make certain that the sample is representative of the air breathed by the workers, and of the daily fluctuations which may occur.

4.4.3 Continuous recording instruments, arranged to give audible and visible signals when a predetermined concentration of trichloroethylene vapor in air is reached, are available.

4.4.4 Testing methods are described in the following references:

Flame Test Method, Using the Halide Torch:

V. A. Stenger et al., *Ind. Eng. Chem., Anal. Ed.*, 11:121 (1939)

F. H. Goldman, *J. Ind. Hyg. & Toxicol.*, 25:181 (1943)

Thermal Decomposition Method:

J. C. Olsen et al., *Ind. Eng. Chem., Anal. Ed.*, 8:260 (1936)

H. F. Smyth, *Ind. Eng. Chem., Anal. Ed.*, 8:379 (1936)

H. Eikins et al., *J. Ind. Hyg. & Toxicol.*, 19:474 (1937)

B. D. Tebbens, *J. Ind. Hyg. & Toxicol.*, 19:204 (1937)

W. F. von Oettingen, *J. Ind. Hyg. & Toxicol.*, 19:413 (1937)

Vapor Pressure Method:

C. Couchman et al., *J. Ind. Hyg. & Toxicol.*, 21:256 (1939)

K. Kay et al., *J. Ind. Hyg. & Toxicol.*, 21:264 (1939)

L. Silverman et al., *J. Ind. Hyg. & Toxicol.*, 21:270 (1939)

Gas Interferometer Method:

F. A. Patty, *J. Ind. Hyg. & Toxicol.*, 21:469 (1939)

G. Harrold et al., *J. Ind. Hyg. & Toxicol.*, 21:491 (1939)

Adsorption Method:

W. Cook et al., *J. Ind. Hyg. & Toxicol.*, 18:194 (1936)

L. Cralley et al., *J. Ind. Hyg. & Toxicol.*, 25:172 (1943)

Photometric Method:

V. F. Hanson, *Ind. Eng. Chem., Anal. Ed.*, 13:119 (1941)

Colorimetric Method:

H. M. Barrett, *J. Ind. Hyg. & Toxicol.*, 18:341 (1936)

See also American Standards Association, "Allowable Concentration of Trichloroethylene", Approved Aug. 6, 1946, Z37.19—1946. (200 ppm).

5. EMPLOYEE SAFETY

5.1 EMPLOYEE EDUCATION AND TRAINING

Safety in handling trichloroethylene depends, to a great extent, upon the effectiveness of employee education, proper safety instructions, intelligent supervision and the use of safe equipment.

The education and training of employees to work safely and to use the personal protective equipment or other safeguards provided for them is the responsibility of supervision. Training classes for both new and old employees should be conducted periodically to maintain a high degree of safety handling procedures. Workers should be thoroughly informed of the hazards that may result from improper handling of trichloroethylene. They should be cautioned to prevent spills and thoroughly instructed regarding proper action to take in case they occur. Each employee should know what to do in an emergency and should be fully informed as to first aid measures.

In addition to the above, employee education and training should include the following:

(a) Instruction and periodic drill or quiz regarding the locations of safety showers, eye baths, bubbler drinking fountains, or the closest source of water for use in emergencies.

(b) Instructions to avoid all unnecessary inhalation of vapors of trichloroethylene and all direct contact with the liquid.

(c) Instructions to report to the proper authority all equipment failures and/or signs of illness.

5.2 PERSONAL PROTECTIVE EQUIPMENT

5.2.1 Availability and Use

While personal protective equipment is not an adequate substitute for good, safe working conditions, adequate ventilation, and intelligent conduct on the part of employees working with trichloroethylene, it is, in many instances, the only practical means of protecting the worker.

particularly in emergency situations. One should keep firmly in mind that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area may be exposed to danger.

The correct usage of personal protective equipment requires the education of the worker in proper employment of the equipment available to him. Under conditions which are sufficiently hazardous to require personal protective equipment, its use should be supervised and the type of protective equipment selected should be capable of control over any potential hazard.

The following personal protective equipment should be used when indicated.

5.2.2 Eye Protection

Chemical Safety Goggles: Cup-type or rubber framed goggles, equipped with the approved impact resistant glass or plastic lenses, should be worn whenever there is danger of trichloroethylene coming in contact with the eyes. Goggles should be carefully fitted by adjusting the nose piece and head band to ensure maximum protection and comfort.

Spectacle-Type Safety Goggles: Metal or plastic rim safety spectacles with unperforated side shields which can be obtained with prescription safety lenses or suitable all plastic safety goggles may be used where continuous eye protection is desirable, as in laboratories. These types, however, should not be used where complete eye protection against trichloroethylene is needed.

Face Shields: Plastic shields (full length, eight inch minimum) with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of material striking the eyes from underneath or around the sides of the face shield.

5.2.3 Respiratory Protection

Severe exposure to trichloroethylene may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection as described below.

NOTE: Respiratory protective equipment must be carefully maintained, inspected, cleaned

and sterilized at regular intervals, and always before use by another person.

(a) *Self-contained Breathing Apparatus* which permits the wearer to carry a supply of oxygen or air compressed in the cylinder, and the self-generating type which produces oxygen chemically, allow for greater mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air or oxygen supply carried. No cylinder (or compressed) oxygen should be used in tanks or other confined spaces.

(b) *Positive Pressure Hose Masks* supplied by externally lubricated blowers. Since these masks depend on a remote air supply, they should be used only where conditions will permit safe escape in the event of air supply failure. Care must be taken to locate the blower air source in an area which is free of air contaminants.

(c) *Air-line Masks* supplied by plant compressed air are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. Such masks should be used only in conjunction with a suitable reducing or demand-type valve, excess pressure relief valve, and filter. The compressed air should be checked frequently to make certain that harmful gases from the decomposition of the lubricating oil used in the compressor, or impure air supply, are not present.

(d) *Industrial Canister Type Gas Masks*, equipped with full face pieces and approved by the U.S. Bureau of Mines, fitted with the proper canister for absorbing trichloroethylene vapor, will afford protection against concentrations of trichloroethylene not exceeding 2 per cent by volume when used in accordance with the manufacturer's instructions. The oxygen content of the air must not be less than 16 per cent by volume. The masks should be used for relatively short exposure periods only. They may not be suitable for use in an emergency since, at that time, the actual vapor concentration is unknown and it may be very high. The wearer must be warned to leave the contaminated area immediately on detecting the odor of a harmful vapor; this is an indication that the mask is not functioning properly or that the vapor concentration is too high.

NOTE: Where carbon monoxide may be encountered in addition to trichloroethylene, the mask should be equipped with an "all purpose canister" and a "timing device" as approved by the U.S. Bureau of Mines.

5.2.4 Head Protection

"Hard" hats should be worn where there is danger from falling objects. If hard hats are not considered necessary, soft-brimmed hats or caps may be worn to give protection against liquid leaks and splashes.

5.2.5 Foot Protection

NOTE: Trichloroethylene attacks natural rubber.

Safety shoes with built-in steel toe caps, and made of leather or some suitable impervious material such as Neoprene, are recommended for workers handling containers of trichloroethylene. Overshoes of a similar suitable material may be worn over leather safety shoes. Footwear should be thoroughly cleaned and ventilated after contamination.

5.2.6 Body, Skin and Hand Protection

Sustained or intermittent skin contact with liquid trichloroethylene may produce dermatitis at the site of contact. It is imperative that contaminated clothing be removed promptly and laundered or thoroughly dried before re-use. Affected areas of the body should be washed thoroughly with soap and water (except the eyes). As a general hygienic measure, facilities for personal cleanliness should be provided and washing before lunch and at the end of the work day should be encouraged.

Clothing made of neoprene or other impervious material may be worn to protect the body against trichloroethylene splashes. These garments must be cleaned inside and out each time they are used.

6. FIRE FIGHTING

As stated in Section 3.2, fires involving trichloroethylene are unlikely, but if they do oc-

cur, they may be controlled by carbon dioxide, dry chemical or foam.

7. HANDLING AND STORAGE

7.1 USUAL SHIPPING CONTAINERS

Trichloroethylene is not regulated by the Interstate Commerce Commission.

7.1.2 Type and Size

Tank cars:

ICC 103, up to 10,000 gallons capacity.

Tank trucks:

ICC Specifications MC 300, MC 301, MC 302, MC 303 or MC 304.

Metal drums:

ICC Specifications 17E, or CFC Rule 40, Section 5C, 55 gallon maximum.

7.1.3 Labeling and Identification

7.1.3.1 Each container should carry an identifying label or stencil.

7.1.3.2 The Manufacturing Chemists' Association recommends that all containers of

trichloroethylene should bear a label as shown on p. 10 in addition to, or in combination with any label, warning or other statement required by statutes, regulations or ordinances.

7.2 DRUMS

7.2.1 Drums should be unloaded carefully to prevent damage. Do not drop or bump.

7.2.2 Each shipment should be examined carefully for leaking drums. If any are found, they should be handled with particular care by turning leak up to prevent further leakage, and should be removed to a safe place where the leakage can be stopped by tightening the plug or by some other approved method.

7.2.3 Before emptying contents, substantially support the drums and block them to prevent movement.

7.2.4 A satisfactory method of removing trichloroethylene from drums is by means of a rotary pump. If emptied by gravity, the drum should be placed on a rack and a faucet inserted in the end bung. Faucets should have

TRICHLOROETHYLENE

WARNING! VAPOR HARMFUL

Use only with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.
Avoid prolonged or repeated contact with skin.
Do not take internally.

MCA Chemical Safety Data Sheet available.

short shanks threaded with Briggs standard straight iron pipe threads and preferably self-closing. A resilient gasket of suitable material should be used to ensure a tight fit. Bung opening and faucet must have the same type and number of threads per inch (MCA Manual Sheet D-32). Protect workmen from vapor and liquid (See 5.2).

7.2.5 To remove the body plug, place bung up, and use a bung or plug wrench. Stand to one side and face away during the operation. After the plug starts, give one full turn. If accumulated internal pressure vents, allow it to reduce to atmospheric pressure; then only should the plug be loosened further or removed.

7.2.6 Before returning shipping containers to suppliers, observe usual precautions regarding complete drainage of contents and properly close all openings.

7.3 TANK CARS

7.3.1 Unloading

7.3.1.1 Unloading operations should be conducted by carefully instructed, reliable employees under adequate supervision (See 5.1).

7.3.1.2 Shipper's instructions should always be followed and all caution markings on both sides of tank and dome should be read and observed.

7.3.1.3 The train or engine crew should accurately spot the car at the unloading line. The unloading track should be level.

7.3.1.4 Car number should be compared with that on shipping papers or invoice to verify contents of car and avoid mixing of products.

7.3.1.5 It is considered good practice that derrails be placed at the open end or ends of the unloading track approximately one car-length from the car being unloaded; unless the car is protected by a closed and locked switch or gate.

7.3.1.6 The hand-brake should be set and standard rail clamps should be installed to block the wheels at the time of unloading. Metal "CAUTION" signs should be fastened to the track. Signs should be 12" x 15", painted light blue. Use the legend "STOP TANK CAR CONNECTED", with the letters in "STOP" four inches high. Signs are available from safety equipment dealers.

7.3.1.7 Tank cars should be unloaded through the dome connection, preferably by pump.

7.3.1.8 If necessary to discontinue unloading a tank car for any reason, all unloading connections must be disconnected. All valves must first be tightly closed, and the closures of all other openings securely applied.

7.3.2 Return Precautions

7.3.2.1 As soon as the tank car is completely unloaded all valves must be made tight, the unloading connections removed, and all other closures made tight, except the heater coil connection and steam connections.

7.3.2.2 Empty tank cars should be returned as promptly as possible, in accordance with instructions received from the shipper. The shipper's routing instructions should always be strictly followed.

7.4 TANK TRUCKS

7.4.1 Ordinarily all operations concerning the tank truck and its appurtenances (fittings,

pumps, hose, etc.) are the responsibility of the driver. Therefore unloading operations should be carried out by reliable and properly instructed employees in cooperation with the driver.

7.4.2 The shipper should be consulted for details on proper unloading procedure.

7.4.3 Before unloading a truck, the engine should be stopped and not started again during the entire unloading operation unless it is necessary to operate the pump by power take-off.

7.4.5 Truck brakes should be set and, if necessary, the wheels blocked.

7.4.6 It is preferable that truck unloading facilities be level and paved and so located that the truck can be easily and safely maneuvered to the unloading spot.

7.4.7 Air pressure should never be used for unloading tank trucks.

7.5 STORAGE

7.5.1 Corrosion

Under normal conditions, trichloroethylene may be stored satisfactorily in galvanized iron, black iron, or steel equipment. Aluminum is unaffected by trichloroethylene but is not generally recommended for storage equipment because of its possible use for some of the other more active chlorohydrocarbons which may react explosively with aluminum under certain conditions.

7.5.2 Drums

7.5.2.1 Drums of trichloroethylene should be stored in a cool place, bung up. To prevent evaporation losses, bungs should be kept tight at all times.

7.5.2.2 Ventilation should be provided at the floor level, as well as in the usual higher locations. Note that vapor is 4.54 times heavier than air (See 2.2). Do not store in pits, depressions, basements, or unventilated areas.

7.5.3 Tanks

7.5.3.1 Each tank, either vertical or horizontal, should have a top and bottom manhole at least 22 inches in diameter, in addition to filling, vent, and measuring device openings, which should be 2 inch flanged connections in the top of the tank. A 2 inch or 2½ inch bottom outlet should be provided for use as a drain during clean-out operations. Vertical tanks should be of the closed top design, and the top should be caulked or welded vapor-tight.

7.5.3.2 Each storage tank should have a vent of diameter at least equal to that of the fill pipe or discharge pipe, whichever is the larger, to permit the escape of vapor during filling. Vents from indoor tanks should terminate outdoors, in such a location that escaping vapor will not contaminate any work space air. The vent is usually protected against entry of moist air by being extended down over the side of the tank into a chamber filled with lump calcium chloride for removal of moisture in the air. It is recommended that a tee be provided in this line above the dryer so that a mercury seal ½ inch deep can be installed as a safety vent in case the dryer plugs from excess moisture. Do not allow mercury to be spilled in any work space. Avoid open mercury surfaces in work spaces.

7.6 SPILLS AND LEAKAGE

7.6.1 Spills should be cleaned up immediately. Employees performing this work should wear adequate personal protective equipment (See 5.2).

7.6.2 Rags or mops wet with trichloroethylene should be placed in closed containers or in a safe place out of doors until they can be dried safely.

7.6.3 Clothing wet with trichloroethylene should be removed immediately. The clothing should not be used again until dry and free of the odor of trichloroethylene. Dry clothing out of doors or in a properly ventilated area.

7.7 REPACKAGING AND BLENDING

7.7.1 Repackaging should be done with adequate attention to the health hazards involved (See 10.).

7.7.2 A label on small containers may be required by State statutes, regulations, or ordinances (See 7.1.3).

7.7.3 Trichloroethylene may be added to flammable solvents to form less flammable or relatively nonflammable mixtures. It should be noted, however, if the flammable solvent is less volatile than trichloroethylene, the mixture will tend to become more and more flammable on evaporation.

7.7.4 When trichloroethylene is added to other solvents, the health hazard of each of the constituents of the mixture must be given careful consideration.

7.7.5 The addition of other products to trichloroethylene may affect its corrosive properties.

8. TANK AND EQUIPMENT CLEANING AND REPAIRS

(HAZARDS AND THEIR CONTROL)

This work is probably the most hazardous of all operations which involve the use or handling of trichloroethylene in industry. All precautions pertaining to education, protective equipment and health hazards should be reviewed and understood.

8.1 PREPARATION OF TANKS AND EQUIPMENT

8.1.1 Tank and equipment cleaning should be under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of the work.

8.1.2 Tanks and equipment, pumps, lines and valves should always be drained and thoroughly flushed with water before being repaired. Workmen should never be allowed to attempt to repair equipment while it is in operation and the lines full. If pipe sections are to be removed and flanges opened, the lower bolts should be loosened first and although the lines have been flushed, care should be taken to avoid personal contact with the liquid draining, or dripping from the equipment. All spillage from the lines or equipment should be removed immediately.

8.1.3 The tank or equipment to be repaired should first be emptied of all liquid, and all pipes leading to and from the tank (except vents) after draining should be disconnected or blanked off. Agitator motor line switches should be locked open.

8.1.4 The tank should be steamed to remove residual trichloroethylene and vapors. Steam lines should be large enough to raise the tank temperature above the boiling point of trichloroethylene (87°C.) and the steaming should be continued until the trichloroethylene vapors have been removed.

8.1.5 The tank should then be cooled, preferably by filling with water and draining once or twice.

NOTE: The volatilized trichloroethylene in the steam effluent should be controlled so as to avoid contaminating the air in the work area in excess of safe limits (See 4.3).

8.1.6 The tank should then be purged with fresh air and the air should be tested for tri-

chloroethylene vapor and for oxygen content before permitting personnel to enter (See 4.4).

8.2 ENTERING TANK

8.2.1 No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested and found to be safe. Furthermore, no workman should enter a tank or vessel that does not have a manhole opening large enough to admit a person wearing a safety harness, life line, and emergency respiratory equipment. It should be ascertained that the tank or vessel can be left by the original entrance.

8.2.2 One man on the outside of the tank should keep the men in the tank under observation and another man should be available nearby to aid in rescue if any of the men in the tank are overcome (See 8.3).

8.2.3 A supplied air respirator or self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank (See 8.3).

8.2.4 Special ventilation is recommended during the entire time men are cleaning, repairing, or inspecting the tank. Ventilation can be accomplished by exhausting or removing vapors from the bottom of the tank either through its bottom openings, or by exhausting the vapors from the tank bottom by means of a large flexible duct where tanks have a top opening only. On tanks having only a top opening, care must be exercised to ensure complete removal of vapors from the entire tank. Care must also be taken to avoid having exhaust gases recycled into the tank.

8.2.5 During the course of the work, frequent tests (See 4.4) should be made to determine that the atmosphere in the tank is being maintained within the safe range. This precaution is necessary because residues not completely removed by washing may recontaminate the tank atmosphere.

8.2.6 In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

8.3 EMERGENCY RESCUE

Under no circumstances should a rescuer enter a tank to remove a victim of over-exposure without proper respiratory protection, a safety harness and an attached life line. The free end of the life line should be manned by an attendant located outside the tank. Another attendant should be immediately available to assist in the rescue if needed. The rescuer should be in view of the outside attendant at all times or in constant communication with him.

8.4 EXTERIOR REPAIR WORK

8.4.1 Exterior tank repairs, including re-

pairs to steam coils, cutting, riveting and welding, should be permitted only after thorough cleaning and testing of the tank to make sure it is free of vapors and after a work permit has been issued by an authorized person.

8.4.2 All outside welding or burning on tanks or equipment which have contained trichloroethylene should be done only after such containers have been completely purged with steam. Purging should be continued while the repair work is in progress.

8.4.3 In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

9. WASTE DISPOSAL

9.1 Waste disposal of trichloroethylene depends to a great extent upon local conditions. Be sure that all Federal, State and local regulations regarding health and pollution are followed. The supplier will be able to furnish

good advice on this matter.

9.2 Residue may be poured on dry sand, earth, or ashes at a safe distance from occupied areas and allowed to evaporate into the atmosphere.

10. MEDICAL MANAGEMENT

10.1 HEALTH HAZARDS

10.1.1 Trichloroethylene may be harmful by inhalation, by contact with skin or mucous membranes, or when taken by mouth. However, if proper precautions are constantly observed, this compound may be handled with safety. Prolonged, excessive, or repeated exposures to the liquid, or to atmospheric concentrations of the vapor above those recommended below are hazardous.

10.1.2 The signs and symptoms of too great exposure to trichloroethylene are the result of action upon the central nervous system, or irritation of the skin, or the respiratory tract. In contrast to chloroform and carbon tetrachloride, injuries to the liver and kidneys are rare, if indeed they ever occur from industrial exposure.

10.1.3 Trichloroethylene is essentially an anesthetic. When inhaled or when taken by mouth, the clinical picture may range from slight irritation of the mucous membranes through all stages of the production of anesthesia. The stage reached depends upon the concentration inhaled, or the quantity swallowed.

10.1.4 The generally accepted Maximum Allowable Concentration of trichloroethylene in the air is 200 ppm. by volume for an 8-hour day. When exposed to higher concentrations, work-

ers may complain of tears and burning of the eyes and irritation of the nose and throat. They may, also, experience nausea and vomiting, drowsiness, acquire an attitude of irresponsibility and behave in a manner resembling any stage of alcoholic intoxication.

10.1.4.1 Acute Poisoning

When a worker inhales an excessive amount of trichloroethylene vapor within a short period of time, the symptoms are essentially those of production of anesthesia. There may be, at first, irritation of the eyes, nose and throat, then dizziness, nausea, vomiting and gradual suppression of consciousness. The picture which develops depends upon the concentration inhaled and the duration of inhalation. If the concentration is high and inhalation prolonged, there will eventually be complete suppression of pain sense and almost complete loss of muscular activity. After a period of very rapid breathing, the respiration and circulation may fall and death follow. High concentrations of trichloroethylene may prevent proper utilization of the oxygen of the blood by the tissues. When this condition is present, physical activity may lead to severe or even fatal circulatory failure.

Some conditions under which acute poisoning may occur are as follows:

(a) By accident, such as equipment failure,

(b) When workers enter enclosures or tanks without having taken adequate precautions (See 8),

(c) When trichloroethylene is handled carelessly (See 5.1).

10.1.4.2 Subacute Poisoning

Subacute trichloroethylene poisoning may result from prolonged or repeated work in an atmosphere containing high concentrations of trichloroethylene but under conditions in which the amount absorbed is not sufficient to cause loss of consciousness.

Workers with subacute poisoning may become acutely ill and suffer from headaches, fatigue, nausea, vomiting, mental confusion and visual disturbances. There may be nerve paralysis affecting nerves to the face or to the extremities. These are part of the development of anesthesia. In some cases, after repeated exposure, a craving seems to develop so that the worker seeks further exposure and becomes an addict. In others, there may be definite action on the heart muscle producing irregular beats of the heart or rapid but inefficient contraction of the heart chambers. In rare cases, this has caused death.

Some of the conditions under which subacute poisoning might occur in employees are as follows:

(a) When the ventilation is inadequate, resulting in high concentrations of trichloroethylene,

(b) When vapor concentrations are high intermittently, due to faulty handling of the liquid,

(c) Failure of the individual to observe precautionary measures,

(d) When an acute exposure of high concentration is superimposed upon prolonged exposure to mild concentrations, circulatory failure can occur.

10.1.5 Toxic Effects from External Contact

10.1.5.1 Skin

Trichloroethylene may cause dermatitis after repeated or prolonged contact with the skin, as occurs in prolonged or repeated handling of rags wet with the chemical product, dipping the hand into the liquid and wearing clothing saturated with it. Frequent contact of the solvent with the skin dries it by removal of the skin oils and makes it rough and red and subject to cracking. This can lead to sec-

ondary infection. If trichloroethylene, or its vapors are trapped between the clothing and the skin, there may be particularly severe action. Reddening, burning and blisters may follow such exposure.

10.1.5.2 Eyes

Trichloroethylene may enter the eyes either as a vapor or as a liquid (spray or splash). The irritation may cause lachrymation, burning and other symptoms. If the eyes are not promptly washed, serious eye damage may occur.

10.1.6 Toxic Effects After Oral Intake

The initial symptoms after toxic amounts of trichloroethylene are taken by mouth are those of irritation of the gastrointestinal tract, such as nausea and vomiting and, perhaps, diarrhea. Then, may follow all the stages of production of anesthesia with the same symptomatology as is produced by inhalation of the compound. In addition, when trichloroethylene is swallowed, kidney function may be completely suppressed.

10.2 PREVENTIVE HEALTH MEASURES

The most important factor in prevention of injury by trichloroethylene is to have sufficient ventilation to keep the concentration of the vapor in the air below 200 ppm. by volume. The odor of trichloroethylene is distinct and most people can notice it at concentrations of the order of 50 ppm.

10.2.1 Personal Hygiene

Employees should be instructed to report any signs or symptoms of a substandard physical condition and receive medical attention.

Those working regularly with trichloroethylene may well be provided with a folder explaining the dangerous properties of this material and a statement of proper precautions to observe.

Facilities for personal cleanliness should be provided and time allowed for thorough washing before lunch and at the end of the work day.

Careful cleansing with mild soap, followed by the use of an oily cream containing lanolin to replace skin oils which may have been dissolved by trichloroethylene, is an important aid in preventing dermatitis.

10.2.2 Physical Examinations

10.2.2.1 Preplacement Examination

Certain individuals have been found who are unduly susceptible to various chlorinated

hydrocarbons, as shown by previous experiences. The exposure of such individuals can be minimized by a careful preplacement physical examination. Exposures to trichloroethylene even in concentrations known to be non-hazardous to normal individuals should be prohibited in the following cases:

- (a) Alcoholics,
- (b) Exceedingly fleshy individuals,
- (c) Undernourished individuals,
- (d) Those with pulmonary diseases, stomach ulcers, high blood pressure, diseases of the liver, kidney, or heart, and

(e) Those suffering from paralysis, convulsive seizures and highly nervous states.

10.2.2.2 Periodic Health Examinations

Employees who are exposed regularly to trichloroethylene should be examined, at least semiannually, by a physician acquainted with the occupational hazards involved. Physical examinations should be required also when any symptoms of poisoning such as enumerated above are present in employees. Discovery of symptoms of trichloroethylene poisoning may indicate some defect in operation. This would serve as an indication to examine other exposed employees for early signs of poisoning.

11. FIRST AID

11.1 GENERAL PRINCIPLES

Most important in the case of any poisoning is quick removal from exposure. In the case of trichloroethylene poisoning, this means first removing the patient from the contaminated atmosphere and, insofar as possible, removing the trichloroethylene from the patient's respiratory tract, skin, or gastrointestinal tract.

Give the patient fresh air by moving him to a well ventilated room and by dispersing any crowd. If breathing has ceased, start artificial respiration at once.

During recovery from an anesthetic dose of trichloroethylene, there may be great excitement. Keep the patient quiet and comfortably warm, but not hot.

Call a physician immediately, explaining briefly and clearly what has happened and the exact location of the patient. *Do not give anything by mouth to an unconscious patient.*

11.2 SPECIFIC ACTIONS

11.2.1 Inhalation

A person showing symptoms of trichloroethylene vapor poisoning should be removed promptly from the contaminated area. In case breathing has stopped, effective artificial respiration, such as that obtained by the arm lift-back pressure method should be started immediately. If oxygen inhalation apparatus is available, oxygen should be administered only if one familiar with the operation of the apparatus is present to administer it. If patient is conscious, hot tea or coffee may be given as a stimulant.

Adrenalin should never be given to a person suffering from trichloroethylene poisoning. A physician should be called at once.

11.2.2 Skin Contact

All contaminated clothing should be removed at once. Clothing, including shoes, soaked in trichloroethylene should be removed and not worn again until thoroughly dry. All affected areas should be washed thoroughly with warm water and soap. After this an ointment containing lanolin should be applied in order to replace the natural skin oils. For serious or persistent cases of skin trouble and for signs and symptoms of generalized poisoning, a physician should be consulted.

11.2.3 Contact with Eyes

If liquid trichloroethylene has entered the eyes, they should be washed promptly with copious quantities of water for at least 15 minutes. It is advisable to irrigate the eyes gently with water at room temperature in order to minimize additional pain and discomfort. Medical attention should be obtained.

11.2.4 Taken Internally

If a person has swallowed trichloroethylene, he should be made to vomit by drinking a glassful of mustard water, lukewarm salt water, or soapy warm water. If necessary, the patient should be encouraged to stick his finger down his throat to induce vomiting. This procedure should be repeated at least three times and then followed by the administration of a tablespoonful of Epsom salt. A physician should be called at once.

The medical information in this publication has been supplied by the Medical Advisory Committee of the Manufacturing Chemist's Association.

CHEMICAL SAFETY DATA SHEETS

*Acetaldehyde	(1952)	SD-43
Acetic Acid	(1951)	SD-41
Acetic Anhydride	(1962)	SD-15
*Acetone	(1962)	SD-87
Acetylene	(1957)	SD-7
*Acrolein	(1961)	SD-85
*Acrylonitrile	(1964)	SD-31
Aluminum Chloride	(1956)	SD-62
Ammonium Dichromate	(1952)	SD-45
*Ammonia Anhydrous	(1960)	SD-8
*Ammonia Aqua	(1947)	SD-13
*Aniline	(1963)	SD-17
Antimony Trichloride (Anhydrous)	(1957)	SD-66
Arsenic Trioxide	(1956)	SD-60
*Benzene	(1960)	SD-2
*Benzyl Chloride	(1957)	SD-69
Benzoyl Peroxide	(1960)	SD-81
Betanaphthylamine	(1949)	SD-32
Boron Hydrides	(1961)	SD-84
*Bromine	(1952)	SD-49
*Butadiene	(1954)	SD-55
*n-Butyllithium in Hydrocarbon Solvents	(1966)	SD-91
*Butyraldehydes	(1960)	SD-78
Calcium Carbide	(1967)	SD-23
Carbon Disulfide	(1967)	SD-12
Carbon Tetrachloride	(1963)	SD-3
*Caustic Potash	(1947)	SD-10
*Caustic Soda	(1968)	SD-9
*Chlorine	(1960)	SD-80
Chloroform	(1962)	SD-89
*Chlorosulfonic Acid	(1949)	SD-33
Chromic Acid	(1952)	SD-44
*Cresol	(1952)	SD-48
*Cyclohexane	(1957)	SD-68
*Diethylenetriamine	(1959)	SD-76
*Dimethyl Sulfate	(1966)	SD-19
Dinitrotoluenes	(1956)	SD-93
*Ethyl Acetate	(1953)	SD-51
*Ethyl Chloride	(1953)	SD-50
*Ethyl Ether	(1965)	SD-29
*Ethylene Dichloride	(1947)	SD-18
*Ethylene Oxide	(1951)	SD-38
Formaldehyde	(1960)	SD-1
*Hydrochloric Acid	(1951)	SD-39
Hydrocyanic Acid	(1961)	SD-67
*Hydrofluoric Acid	(1957)	SD-25
*Hydrogen Peroxide	(1955)	SD-53
Hydrogen Peroxide (Not Exceeding 52%)	(1961)	SD-53—Sup. A
Hydrogen Peroxide (High Strength)	(1961)	SD-53—Sup. B
Hydrogen Sulfide	(1968)	SD-36
*Isopropylamine	(1959)	SD-72
Lead Oxides	(1956)	SD-64
Maleic Anhydride	(1962)	SD-88
Methyl Acrylate and Ethyl Acrylate	(1960)	SD-79
*Methanol	(1948)	SD-22
Methylamines	(1955)	SD-57
*Methyl Bromide	(1968)	SD-35
*Methyl Chloride	(1951)	SD-40
Methylene Chloride	(1962)	SD-86
*Methyl Ethyl Ketone	(1961)	SD-83
*Mixed Acid	(1956)	SD-65
Naphthalene	(1956)	SD-58
*Nitric Acid	(1961)	SD-5
*Nitrobenzene	(1967)	SD-21
Ortho-Dichlorobenzene	(1953)	SD-54
Paraformaldehyde	(1960)	SD-6
paraNitroaniline	(1966)	SD-94
Perchloroethylene	(1948)	SD-24
Perchloric Acid Solution	(1965)	SD-11
*Phenol	(1964)	SD-4

Phosgene	(1967)	SD-95
Phosphoric Acid	(1958)	SD-70
Phosphoric Anhydride	(1948)	SD-28
*Phosphorus, Elemental	(1947)	SD-16
*Phosphorus Oxychloride	(1948)	SD-26
*Phosphorus Pentasulfide	(1958)	SD-71
*Phosphorus Trichloride	(1948)	SD-27
Phthalic Anhydride	(1956)	SD-61
Propylene	(1956)	SD-59
Sodium Chlorate	(1952)	SD-42
Sodium Cyanide	(1967)	SD-30
*Sodium, Metallic	(1952)	SD-47
Sodium and Potassium Dichromates	(1952)	SD-46
Styrene Monomer	(1951)	SD-37
Sulfur	(1959)	SD-74
Sulfur Chlorides	(1960)	SD-77
*Sulfur Dioxide	(1953)	SD-52
*Sulfuric Acid	(1963)	SD-20
Tetrachloroethane	(1949)	SD-34
*Toluene	(1956)	SD-63
Toluidine	(1961)	SD-82
Toluene Diisocyanate	(1959)	SD-73
1, 1, 1-Trichloroethane	(1965)	SD-90
Trichloroethylene	(1956)	SD-14
*Vinyl Acetate	(1959)	SD-75
*Vinyl Chloride	(1954)	SD-56
Zirconium and Hafnium Powder	(1966)	SD-92

* Chem-Cards available

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TC-3 Tank Cars—Unloading when filled with liquid Caustic Soda or Caus- tic Potash (Revised 1946, 1950, 1952)	.20
TC-4 Tank Cars—Unloading when filled with flammable liquids (Revised, 1952)	.20
TC-6 Tank Cars—Unloading when filled with Phenol (Revised, 1959)	.30
TC-7 Tank Car Approach Platforms	.20

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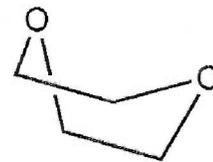
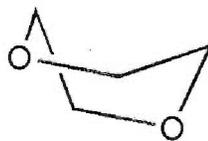
Butyllithium	Methyl
Chlorine Trifluoride	Methacrylate
Diethylamine	Monomethyl
(Anhydrous)	Hydrazine
Dimethyl Ether	Motor Fuel
Epichlorohydrin	Antiknock
Ethanol	Compound
Ethyl Acrylate	Nitric Acid
Fluorine (Liquid)	(Red, Fuming)
Formic Acid	Nitrogen, Liquid
Hydrazine/UDMH	Nitrogen Tetroxide
Hydrogen, Liquid	Oleum
Isopropanol	Oxygen, Liquid
Isopropyl Ether	Pentaborane
Methyl Acrylate	Perchloryl Fluoride
Methylamines	Sulfur Trioxide
(Anhydrous)	Unsymmetrical
Methylamines	Dimethyl
(Aqueous)	Hydrazine
Methyl Isobutyl	Vinylidene Chloride
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Santa Clara Valley
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1,4-Dioxane

and other

SOLVENT STABILIZERS

WHITE PAPER

June 14, 2001

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Introduction

Industrial solvents used in degreasing, electronics, metal finishing, fabric cleaning, and many other applications are commonly formulated with additives to enhance their performance. These additives, known as *solvent stabilizers*, serve to prevent solvent breakdown and to inhibit reactions that may degrade solvent properties. Many solvent stabilizer compounds are present at volumetrically inconsequential proportions to be considered significant for solvent release site investigation and cleanup. One ether stabilizer, 1,4-dioxane, has been included with 1,1,1-trichloroethane (TCA, also called methyl chloroform) in mixtures at 2 to 8% by volume, and has proven to be a contaminant of concern at solvent release sites. Other solvent stabilizer compounds may also be problematic. The industrial applications in which solvents are used, such as cold vapor degreasing, tend to increase the proportion of some stabilizers in condensate relative to the host solvent. Once these waste residuals are spilled, leaked, or dumped to the subsurface, 1,4-dioxane tends to be refractory to the biotransformation of TCA, resulting in further increases in the relative proportion of stabilizers.

Solvent stabilizer compounds have thus far received relatively little attention from regulatory caseworkers and remedial project managers at solvent release sites. 1,4-dioxane was not detectable at low concentrations in a standard laboratory scan for chlorinated solvents, and Maximum Contaminant Levels have not been established for this compound. This may explain why solvent stabilizer compounds are not routinely analyzed in groundwater at solvent release sites, or included in the cleanup objectives of regulatory orders. It is only within the past few years that improvements to laboratory methods for 1,4-dioxane have made it possible to obtain reliable detections at concentrations comparable to other volatile organic compounds. Familiarity with solvent stabilizer compounds can aid in site investigation, remedial design, forensic investigations, and water supply management.

California's regulatory guidance for 1,4-dioxane is a Department of Health Services Drinking Water Action Level (3 ug/L). 1,4-dioxane is listed as a Class II-B probable human carcinogen, and is known to damage the kidneys. 1,3-dioxolane, an alternative stabilizer for TCA, has similar physical and chemical properties to 1,4-dioxane (see Section 2.1, below); however, it is not listed as a US EPA Clean Water Act Priority Pollutant.

1,4-dioxane is not significantly removed by conventional pump and treat technologies (air stripping and carbon adsorption), and is generally resistant to biodegradation. Advanced oxidation processes, the primary available treatment technology successful in removing 1,4-dioxane from groundwater, is expensive and energy-intensive.

This report summarizes information obtained on solvent stabilizers from an extensive literature review, and presents the nature and use of solvent stabilizers, how they behave in the subsurface, a description of laboratory analytical techniques, a summary of toxicological information for solvent stabilizer compounds, and a survey of the effectiveness and costs of available treatment technologies. Calculations of expected migration rates are contrasted with case study examples. Implications for solvent release site remediation, forensic investigations, and groundwater basin management are also discussed.

1.0 SOLVENT STABILIZERS

Chlorinated solvents sold for use in metal cleaning, degreasing, electronics, and textile cleaning applications require solvent stabilizer compounds to ensure proper performance in the intended application. Without these compounds, solvents tend to break down in the presence of light, heat and oxygen, or react with acids and metal salts.

1.1 Purpose of Solvent Stabilizers

Addition of solvent stabilizers is necessary to supply solvents with acid acceptors, metal inhibitors, and antioxidants.

During the degreasing process, both solvents and oils can decompose and produce strong acids. These acids, usually hydrochloric acid, can corrode the parts being cleaned and the cleaning equipment itself. Acid acceptors react with and chemically neutralize trace amounts of hydrochloric acid formed during degreasing operations. Acid acceptor compounds are either neutral (epoxides) or slightly basic (amines), and react with hydrochloric acid, forming an alcohol in the process (Archer, 1984). If left unneutralized, hydrochloric acid can cause solvent degradation.

Metal inhibitors deactivate metal surfaces and complex any metal salts that might form. Metal stabilizers are Lewis bases that inhibit solvent degradation reactions in the presence of a metal and its chloride (e.g. aluminum and aluminum chloride). The inhibitor either reacts with the active aluminum site, forming an insoluble deposit, or complexes with aluminum chloride, preventing degradation of the solvent.

Antioxidants reduce the solvent's potential to form oxidation products (Archer, 1984). Antioxidants suppress the free radical chain decomposition reaction of unsaturated solvents by forming stable resonance hybrids and slowing the propagation step of auto-oxidation (Joshi et al, 1989).

1.2 Solvent Compositions and Stabilizer Packages

TCE and TCA require both metal inhibitor and acid acceptors, while TCE also requires an antioxidant (Archer 1996). Perchloroethylene (PCE) is relatively stable and requires only minor amounts of acid inhibitors for degreasing operations, but no metal inhibitors (Keil, 1978). Methylene chloride (MC) is also quite stable, requiring less than 0.1% acid inhibitors by volume.

Producers of chlorinated solvents emphasize the stability of their products in their marketing literature. For example: "NEU-TRI™ solvent [a TCE formulation] is highly stabilized for vapor degreasing. Its unique combination of stabilizers makes it especially effective for long-term use. The stabilizer system prevents the build-up of acid in the degreaser and also protects against metal corrosion and reaction in the solvent." (Dow Chemicals, 2001).

Composition of 1,1,1-Trichloroethane

Uninhibited (unstabilized) TCA may react with aluminum to produce aluminum chloride, 2,2,3,3-tetrachlorobutane, 1,1-dichloroethylene; and hydrogen chloride. Adequate metal inhibitors can prevent TCA-aluminum reactivity and allow the solvent to be used in aluminum metal-cleaning applications (Archer, 1979).

The solvent stabilizer packages added to commercially available TCA vary with grade and producer. Actual compositions are difficult to obtain because the formulas are proprietary. Viewing Material Safety Data Sheets (see Table 1.1), a general sense can be obtained for the variation of solvent composition and the inclusion of stabilizer compounds in the formulation. Several producers of TCA now use 1,3-

dioxolane instead of 1,4-dioxane, and some (Great Western Chemical) advertise their product as "Dioxane Free". Many current applications of TCA list 1,3-dioxolane as the stabilizer present at the greatest weight fraction, for example 3% in a cleaning solvent, 3% in "electrical grade silicon bulk", 2-3% in a tire-cleaning solvent, and 3% in a brake-cleaning solvent (Cornell University, 2001 a,b,c,d; Alonso, 2001)

One producer, Occidental Chemical, lists TCE as present in its formulation of TCA, but no weight fraction is specified. All of the MSDS referenced in Table 1.1 were obtained from the Internet in 2001; older formulations may have used different proportions, and discussions with solvent producers provide an anecdotal basis for greater amounts of these additives in past decades (Mertens, 2000; HSIA, 2000). The multitude of synonyms and trade names for the chemicals added to solvents as stabilizers and inhibitors can lead to confusion for non-chemists. Table 1.2 summarizes synonyms of the more common solvent stabilizers.

Table 1.1 Composition of 1,1,1-Trichloroethane from Material Safety Data Sheets

Compound	Fischer	Vulcan	J.T.Baker	PPG	UnoCal Chem	Occ. Chem.	GW Chem.
TCA	95%	>95%	96-100%	95 %	96-98%	96 –97.5%	95%
Nitromethane						0.2 –0.5%	
1,2-butylene oxide		<0.5%	< 0.5%				
1,4-dioxane	~5%		< 3%	+	0-4%	2 – 2.7%	0%
sec-butanol				<2%			1 – 2%
1,3-dioxolane		<3%		<2%			2%

("+" indicates present but weight fraction not specified. From web search for MSDS sheets for currently available formulations; does not reflect compositions of solvents used in past decades)

Table 1.2 Synonyms for Common Solvent Stabilizers

1,4-DIOXANE	1,3-DIOXOLANE	1,2-BUTYLENE OXIDE	TETRAHYDRO FURAN	EPICHLOROHYDRIN
DX 1,4-Diethylene-dioxide diethylene oxide	1,3-dioxolan Glycolformal	1,2-Epoxybutane EBU Propyl Oxirane Epoxybutane	THF 1,4-epoxybutane furanidine Cyclotetra-methylene oxide tetramethylene oxide hydrofuran oxacyclopentane	Chloromethyloxirane glycidyl chloride chloropropylene oxide Glycerol epichlorohydrin 1,2-epoxy-3-chloropropane 3-chloro-1,2-epoxypropane
p-dioxane	dioxolane	2-Ethylloxirane	Oxolane	(chloromethyl)-ethylene oxide gamma-chloropropylene oxide
tetrahydro-1,4-dioxan	Glycol methylene ether	DIMETHYL AMINE	NITROMETHANE	1-chloro-2,3-epoxypropane 2,3-epoxypropyl chloride
Dioxyethylene-ether	dihydroethylene glycol formal formal glycol	DMA	NMT	
Glycoethylene ether		N-methyl-methanamine	Nitrocarbol	

Composition of Trichloroethylene

TCE composition also varies with grade, producer, and intended application, but generally stabilizers comprise less than 1% of TCE. Stabilizers in TCE formulations include a long list of specialty compounds, most of which are not reflected on Material Safety Data Sheets due to the small quantities of additives and the proprietary nature of commercial solvent formulations. Table 1.3 presents a compilation of individual stabilizer compounds added to TCE as listed in the cited references.

Table 1.3 Additives to Trichloroethylene at Concentrations Totalling Less than 1%

Epichlorohydrin	1,2-epoxybutene	2,2,4-trimethylpentene-1
[1,4-dioxane]**	Propanol	Thymol
1,3-dioxolane	diethyl amine	amyl alcohol
Triethylamine	Isoeuganol	Diethanolamine
pentanol-2-triethanolamine	n-methylpyrrole	Isocyanates
styrene oxide	cyclohexene oxide	Diisopropylamine
p-tert-butylphenol	n-ethyl pyrrole	ethyl acetate
Diisobutylene	Thiazoles	Alkoxyaldehyde hydrazones
Pyridine	p-tert-amylphenol	5,5-dimethyl-2-hexene
1,2-propylene oxide	tetrahydrofuran	glycidyl acetate
Tetrahydropyran	Trioxane	n-methylmorpholine
2-methoxyphenol	borate esters	pentene oxide
Morpholine	Aniline	3-methoxy-1,2-epoxy propane
Isocyanates	Butadiene oxide	2-methyl-1,2-epoxypropanol
2,3-epoxy 1-propenol	o-cresol	Nitropropanes
Epoxy cyclopentanol	Stearates	(2-pyrryl)-trimethylsilane
methyl ethyl ketone		
n-methylpyrrole		

Sources: Kircher, 1957, Hardie, 1964, Mertens, 1993, Archer, 1996, Vonder Haar et al, 1994, Joshi et al, 1989, US EPA, 1984. **Primary evidence for the presence of 1,4-dioxane in TCE could not be found by the author or Doherty, 2001, although numerous articles list it as an additive to TCE. Officials at DOW Chemical assert that 1,4-dioxane was not a constituent of TCE (Mertens, 2001). Kircher, 1957, lists "normal ethers and inner ethers" as stabilizers of TCE, but does not explicitly list 1,4-dioxane.

Jackson and Dwarakanath (1999) presented many of these compounds classed by chemical type and purpose, as shown in Table 1.4:

Table 1.4 – TCE Additives classed by chemical type and purpose

Chemical Type	Examples	Purpose
Aliphatic amines	Triethylamine, diisopropyl-amine	Free radical scavengers
Heterocyclic nitrogen compounds	Pyridine, pyrrole, alkyl pyrroles	Antioxidants
Substituted phenols	2-methoxyphenol, cresol	Antioxidants
Oxygenated organics	1,4-dioxane, acetone, butylene oxide, propylene oxide, tetrahydrofuran, epichlorohydrin	Acid acceptors**

(after Jackson and Dwarakanath, 1999) **Jackson and Dwarakanath identify 1,4-dioxane as an acid acceptor, while Joshi et al, 1989, identify it as an aluminum stabilizer in TCA which is not needed in TCE.

Stabilizers are continually depleted during normal degreasing operations. Dow Chemical markets Maxistab™ (packaged stabilizer concentrates) for use with TCE and PCE in vapor degreasing applications. These products are said to boost performance and extend the use of the solvent. A vapor degreasing test kit for monitoring the solvent to determine when new stabilizers are required is also available (DOW Chemical 2001).

Presence of stabilizers in TCE cannot be readily discerned from current MSDS sheets, as the quantities added, often in the parts per million range, do not meet the threshold for listing. Table 1.5 summarizes a review of currently available MSDS Sheets for TCE.

Table 1.5 Composition of Trichloroethylene from Material Safety Data Sheets

Compound	ChemCentral/Kansas	Fisher	New Hermes Neu-TRI (DOW)	Baxter
Trichloroethylene	99.4%	100%	>99%	99%
1,2-butylene oxide (epoxybutane)	0.5%		<1%	1%

Methylene Chloride

Methylene chloride (DCM, also called dichloromethane) is preferred for low-temperature applications, to clean electronic parts with temperature sensitive components. It is generally distributed as 99.9% MC, with stabilizer additives commonly in the parts per million range. Cyclohexane, cyclohexene, amylene, and other olefins and hydrocarbons may be included with DCM to inhibit reactions with metals.

Methylene Chloride is a stable compound when pure and free of moisture, and will not corrode common metals such as mild or galvanized steel, copper, tin, nickel or lead. In contact with free phase moisture, however, DCM may slowly hydrolyze to form acidic by-products that will corrode these metals. The rate of the corrosion process is self-accelerating. Pure DCM absorbs atmospheric moisture slowly but will eventually become saturated.

DCM is less reactive to light metals such as aluminum, magnesium, and their alloys, than many other chlorinated solvents. These metals are naturally insulated from corrosion by the presence of an oxide film. Contact with well-stabilized DCM will not normally produce an adverse reaction. However, if the oxide layer is broken, for example by the metal surface becoming scratched, and the fresh, active metal surface comes into contact with DCM which is unstabilized, or has depleted or inadequate stabilization, a Friedal-Craft reaction can be initiated. Once started, the reaction will proceed rapidly, and in some cases explosively, with the evolution of heat and large quantities of hydrochloric acid (Chlor-chem, 2001).

Perchloroethylene

Perchloroethylene (PCE, also called tetrachloroethylene) does not require a metal inhibitor, but may require acid acceptors for degreasing applications. In the presence of light and air, PCE slowly autooxidizes to trichloroacetyl chloride. Stabilizers, such as amines or phenols, inhibit the decomposition process to extend solvent life and protect equipment and materials. Cyclohexene oxide and butoxymethyloxirane are also listed as inhibitors in PCE (Joshi et al, 1989). Compared to other chlorinated ethanes and ethenes, PCE is relatively stable, and generally requires only small amounts of stabilizers (Keil, 1978).

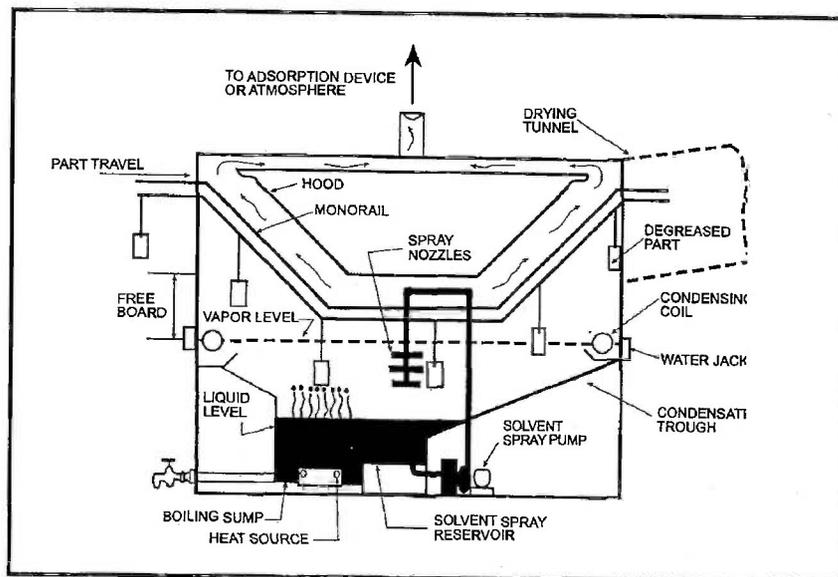
1.3 Relative Proportions of Stabilizers in Vapor Degreasing Waste Residuals

Vapor Degreasing

A vapor degreaser is an enclosed chamber with a solvent reservoir and a heat source to boil the solvent, and a cooling surface to condense the vapor in the upper section. A schematic of a vapor degreasing system is shown in Figure 1.1. Metal objects from which grease will be removed are hung in the air-free zone of solvent vapor. The hot vapor condenses onto the cool parts dissolving oils and greases and providing a continuous rinse in clean solvent (ASTM, 1989; Murphy, 2000).

In vapor degreasing systems, stabilizers partition between the vapor phase and boiling liquid phase according to their boiling points. 1,4-dioxane boils at 101° C while TCA boils at 74°C (see Table 2.1). Systems designed to handle heavy loads of oil and grease are designed to distill the solvent for ongoing purification. In such vapor degreasers, additives such as 1,4-dioxane tend to be concentrated in sludges known as still bottoms. In vapor degreasing systems used by the aerospace industry, still bottoms generated by typical in-process distillation is composed of 70% to 80% solvent and 20 to 30% oil, grease, and solids with traces of water. In electronics industry manufacturing using CFC-113, still bottom compositions of 85 - 95% CFC113 with oil and flux comprising 5 to 15% (Jackson, 1999; Evanoff, 1990). Solvents are also reclaimed using activated carbon; however, this technique selectively sorbs some additives, requiring their reintroduction after reclamation.

Figure 1.1 Typical Vapor Degreaser Configuration



A study on the effects of distillation on solvent stabilizers and inhibitors for different solvents found that distillation significantly concentrates several stabilizers in still bottoms. Tables 1.6a, 1.6b, and 1.6c, below, profile results of this study (Joshi, et al, 1989). For all three solvents studied, stabilizers were retained in still bottoms in excess of 35% of their concentrations in the feed spent solvent. Used TCA showed a 68% increase in the weight fraction of 1,4-dioxane. This study also found that usage in vapor degreasers not equipped with in-process distillation units caused concentrations of several inhibitors and stabilizers to decrease with duration of use.

Table 1.6a Stabilizer Concentrations of Reclaimed Trichloroethylene

Sample	Inhibitor Concentration (weight fraction)			
	Butylene Oxide (x10 ³)	Epichlorohydrin (x10 ³)	Ethyl Acetate (x10 ⁴)	Methyl Pyrrole (x10 ⁴)
New TCE	1.64	1.66	3.46	1.59
Spent TCE	0.685	1.69	2.85	2.18
TCE Distillate	0.718	1.61	2.58	1.66
Carbon Adsorbed TCE	0.44	1.31	2.65	0.90

Table 1.6b Stabilizer Concentrations of Reclaimed Perchloroethylene

Sample	Inhibitor Concentration (weight fraction)	
	Cyclohexene Oxide (x10 ³)	Butoxymethyl Oxirane (x10 ³)
New PCE	1.06	4.26
Used PCE	0.988	7.45
PCE Distillate	0.968	5.42
Carbon Adsorbed PCE	0.091	5.40

Table 1.6c Stabilizer Concentrations of Reclaimed 1,1,1-Trichloroethane

Sample	Inhibitor Concentration (weight fraction)		
	n-methoxy-methanamine ($\times 10^4$)	Formaldehyde dimethyl-hydrazone ($\times 10^3$)	1,4-Dioxane ($\times 10^3$)
New TCA	8.92	5.78	17.2
Used TCA	4.14	6.16	29.0
TCA Distillate	4.60	7.22	19.6
Carbon Adsorbed TCA	1.30	3.37	23.4

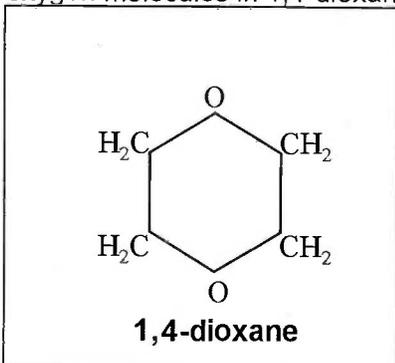
Guidance for operation of vapor degreasers often calls for adding additional solvent to restore solvent performance, thus further concentrating stabilizers in the still bottoms with each addition of new solvent. Waste solvent released to soil and groundwater from improperly disposed still bottoms may therefore have a substantially higher fraction of stabilizers than was originally formulated, particularly in the case of 1,4-dioxane and TCA.

Because vapor-degreasing processes consume solvent stabilizers and inhibitors or concentrate stabilizers in still bottoms, operators may also add stabilizers back into the solvent to ensure the solvent performs as intended. Stabilizer packages such as DOW Chemical's MaxiSTAB are marketed for this purpose. The need to reintroduce stabilizers into spent solvents has bearing for cleanup investigations at solvent recycling facilities, where solvent stabilizer compounds may have been stored in pure form to reconstitute spent solvents.

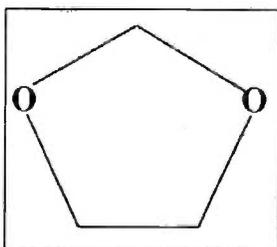
As the use of TCA has been phased out due to laws and taxes intended to reduce ozone depletion, alternative solvents have become available. Alternative vapor degreasing formulations, for example EnSolv Vapor Degreasing & Cleaning Solvent, use n-propyl bromide as an alternative solvent, but also use 3% 1,3-dioxolane as a stabilizer (EnSolv, 1996).

1.4 Chemistry of Solvent Stabilizers

1,4-Dioxane is a cyclic ether, and is also known by the synonyms *p*-dioxane, diethylene ether, diethylene dioxide, and glycol ethylene ether. It is a dimer of ethylene oxide. Dioxane is a Lewis base because the oxygen molecules in 1,4-dioxane have electrons available for sharing (a base is a proton acceptor; a Lewis base is an electron pair donor). The molecular structure of 1,4-dioxane is shown at left. Its two oxygen atoms make it hydrophilic and infinitely soluble in water. Dioxane has no dipole moment owing to the symmetrical position its two oxygen atoms in the chair conformation; in two different boat conformations, 1,4-dioxane has dipole moments of 1.4 and 2.4 (Ledger and Suppan, 1967). Dioxane boils at 101 °C (Windholz et al, 1983).



1,4-Dioxane is made from diethylene glycol by heating and distilling glycol with dehydration catalysts such as sulfuric acid. It can also be manufactured by treatment of bis(2-chloroethyl)ether with alkali, or by dimerization of ethylene oxide (IARC, 1972).



1,3-dioxolane is a stable reaction product of ethylene glycol and formaldehyde. It is a volatile liquid, miscible with water in all proportions. 1,3-dioxolane has a melting point of -95°C, and a boiling point of 78°C. 1,3-dioxolane is also known by the synonyms dioxolane; glycol methylene ether; 1,3-dioxacyclopentane;

glycolformal; 1,3-dioxoledioxolane; dihydroethylene glycol formal; and formal glycol.

1.5 Other Uses of Solvent Stabilizer Compounds in Manufacturing

Approximately 90% of the 1985 1,4-dioxane production in the United States was used as a stabilizer for chlorinated solvents, particularly, TCA (US EPA 1995). Knowledge of other industries using 1,4-dioxane in pure form, or producing 1,4-dioxane as a by-product of manufacturing, may aide in site investigation and forensic geochemical investigations for source apportionment.

1,4-dioxane is used in numerous industrial processes and is included with a variety of consumer and commercial products. Table 1.7 summarizes common applications of 1,4-dioxane. 1,4-dioxane may also occur as a by-product of some manufacturing processes, and as a contaminant in some products.

Table 1.7 Additional Industrial and Commercial Uses of Dioxane

Solvent in paper manufacturing	as a wetting & dispersing agent in textile process
Paints, lacquer, and varnish remover	In microscopy
Stain and printing compositions	as a purifying agent in pharmaceuticals
In liquid scintillation counters	In resins, oils, waxes, and cements
In deodorants, shampoos & cosmetics	In fumigants
Impregnating cellular acetate	as an additive in aircraft deicing fluid formulations
'inert' ingredients of pesticides	as an additive in antifreeze
As a by-product formed during esterification of polyester	

(Sources: Montgomery, 1996; Beernaert et al, 1987; Mackison et al, 1981; US EPA, 1979; ILO, 1979; NCI/DCE, 1985);

Polyethoxyleated surfactants used in detergents may contain dioxane formed during the polymerization of ethylene oxide. (Black et al, 1983; Abe, 1996, US EPA, 1999b). 1,4-dioxane is a contaminant in some surfactant compounds used in herbicides, such as polyoxyethyleneamine in the isopropylamine salt of glyphosate, an ingredient in the most common herbicides (common trade names Roundup, Pondmaster; Rattler; Rodeo) (Briggs et al, 1992; Brooks, et al, 1973). 1,4-dioxane and epichlorohydrin are listed as contaminants of toxicological concern among inert ingredients of pesticides (US EPA, 1989).

Cosmetics containing ethoxylated surfactants may be contaminated by 1,4 dioxane (Scalia et al, 1992). In shampoo manufacturing, 1,4-dioxane is introduced into the product via the use of ethoxylated fatty alcohol sulfates as cleansing agents. During the process of alcohol ethoxylation, ethylene oxide can dimerize to form 1,4-dioxane, which is subsequently carried through the shampoo manufacturing process¹. A variety of commercially available cosmetics, including shampoos, liquid soaps, sun creams, moisturizing lotions, after-shave balms, baby lotions, day creams, and hair lotions, were analyzed for 1,4-dioxane; 56% of the total products investigated contained 1,4-dioxane with levels ranging from 3.4 to 108.4 mg/kg (Italia and Nunes, 1991). 1,4-dioxane is commonly found in treated wastewater effluent and landfill leachate (see Section 2.6, below). Many producers have begun vacuum stripping procedures in their manufacture of the fatty alcohol sulfates to limit contamination of their products by 1,4-dioxane.

¹ For those curious to know whether their sundries may contain 1,4-dioxane, the following is a list of some of the commonly used ethoxylated ingredients in shampoos and other cosmetic products: Sodium laureth sulfate; Ammonium laureth sulfate; Triethanolamine laureth sulfate; Cocamide; Cocamide DEA; ingredients with TEA, MEA, DEA, MIPA, PEG; Polysorbates; Triethanolamine; Sodium C14-16 Olefin Sulfate (Sulphonate); Disodium Oleomido Sulfosuccinate; Cocamidopropyl Betaine; Ammonium Cocoyl Isethionate; Ammonium Lauryl Sulphate; Sodium C12-15 Pareth Sulfonate; Disodium Cocoamphodiacetate. Presence of these ingredients does not equate to presence of 1,4-dioxane, it only establishes an increased likelihood of its presence if vacuum removal of 1,4-dioxane is not employed during manufacturing. Direct testing is the only valid means of verification, and probably is not warranted. 1,4-dioxane has a comparatively low dermal toxicity to laboratory animals (see Section 4.3).

1,4-dioxane is a by-product in the production of polyethylene terephthalate (PET) plastic, and substantial soil and groundwater contamination has occurred at some PET manufacturing facilities and waste sites in North Carolina (Zenker, 2001). 1,4-dioxane is used to impregnate cellular acetate membranes in the production of filters used in reverse osmosis and in laboratory and groundwater sampling filters. The Gelman Sciences facility in Scio, Michigan, which manufactures groundwater sampling filters familiar to groundwater professionals, is the site of one of the nation's largest releases of 1,4-dioxane in groundwater, where the municipal water supply has been impacted (Michigan Department of Environmental Quality, 2001).

1,3-dioxolane

1,3-dioxolane is primarily used for the production of polyacetals and other polymers (rigid plastics). Only 5% is used for other purposes, including stabilizers for halogenated organic solvents (Dioxolane Manufacturers Consortium, 2000).

1.6 History of Solvent and Solvent Stabilizer Production and Use

The following discussion highlights which solvents were preferred for common industrial applications in the past four decades, and accordingly, which stabilizers may have been released from past mishandling of solvent wastes.

TCE was the preferred solvent used in many industrial applications throughout the fifties and sixties. In the late 1960s, TCE came under increasing scrutiny for occupational exposure because it was identified as an animal carcinogen. As a result, many firms switched to TCA. During the late 1980s and early 1990s, many firms using Freon-113 as a solvent converted to TCA as it is a less potent ozone depleter. Because of the current production ban on TCA, some firms are now converting back to TCE.

1,4-dioxane has been produced in commercial quantities by relatively few American manufacturers (Table 1.8). In 1990, between 10.5 and 18.3 million pounds of dioxane were produced in the United States. Approximately 90% of the 1985 1,4-dioxane production was used as a stabilizer for chlorinated solvents, particularly TCA.

Table 1.8 Major American Producers of 1,4-dioxane

Manufacturer	Headquarters Location	Production Location
Ferro Corporation	Cleveland, Ohio	Baton Rouge, Louisiana
CPS Chemical Company Inc.	Old Bridge, New Jersey	New Jersey
Dow Chemical USA	Midland, Michigan	Freeport, Texas

(Source: Stanford Research Institute, 1989)

Table 1.9 Production Data for 1,4-dioxane, Pounds per Year

1973	1974	1975	1976	1977	1982
1,620,485	1,762,775	1,258,150	1,485,683	1,222,467	6,750,000

(Source: United States International Trade Commission, 1994)

The date that a manufacturer began synthesizing a chlorinated solvent is frequently used as evidence regarding when it was available at a facility. This approach assumes that potential suppliers and/or products containing chlorinated solvents are known. Table 1.10 identifies manufacturers of four chlorinated solvents in the United States from 1908 to 2000 (Morrison, 2001, after Doherty, 2000).

Table 1.10 Period of Solvent Production by Manufacturer

MANUFACTURER	TCE	TCA	MANUFACTURER	TCE	TCA
Carbide & Carbon Chemicals	1922-1935	-	Pittsburgh Plate Glass/ PPG Industries	1956-2000	-
Diamond Alkali/ Diamond Shamrock	-	-	PPG Industries	-	1962-2000
Dow Chemical	1921-2000	1936-1994	R&H Industries	1925-1972	-
DuPont Company	-	-	Vulcan materials	-	1970-2000
Ethyl Corporation	1967-1982	1964-1976	Westvaco Chlorine	1933-1949	-
Hooker Chemical/ Occidental Chemical	1956-1980	-	Diamond Shamrock	1969-1977	-
Hooker-Detrex/Detrex Chemical	1947-1972	-	Niagara Alkali	1949-1955	-

(adapted from Morrison, 2001. First compiled by Richard Doherty, and presented on the Internet by Robert Morrison)

1.7 History of Solvent Waste Disposal Practices

Historical handling, storage, and disposal practices for chlorinated solvents and their wastes have resulted in widespread soil and groundwater contamination by solvents. In the Silicon Valley, where accelerated demand for semiconductors and printed circuit boards lead to rapid expansion of the electronics industry in the 1970s, the large quantities of solvents needed for wafer fabrication and parts cleaning. Public safety agencies required that these solvents and solvent wastes be stored in underground tanks. Many of these tanks and associated piping leaked, resulting in numerous instances of soil and groundwater contamination.

Among the oldest citations of solvent contamination of groundwater, the following text is an excerpt from a description of TCE contamination of groundwater in England published in the Analyst, in March of 1949 by F. Kyne and T. McLachlan (cited in Morrison, 2001).

Cases of contamination of wells by trichloroethylene have come to our notice. In the first, the well was situated beside a factory that used large quantities of trichloroethylene as a solvent. During a fire at the factory a tank of the liquid burst and the ground was saturated with the solvent. After more than four years the water in the well still had an odour of trichloroethylene and the well had to be abandoned. The well was sunk in gravel only about 20 feet from a river and one might have expected that the movement of water through the gravel would have removed the contaminant.

In the other case, the well was situated 150 to 200 yards from a pit in an open field where waste trichloroethylene had been dumped. It was in valley gravel and in the direct line of flow towards the river. The water in it had a slight odour of trichloroethylene and was said to cause stomach disorders, giddiness, etc. The amount of trichloroethylene in the water was found to be 18 parts per million when estimated by . . . a modification of the Fujiwara pyridine-sodium hydroxide reaction. From these two cases it is evident that contamination by compounds of this nature is likely to be very persistent and there is some evidence of toxicity at very low concentrations.

Users of chlorinated solvents were routinely advised to dispose of waste solvents by pouring onto the ground or into trenches for evaporation or burning. As we now know, these practices resulted in significant soil and groundwater contamination by still bottoms. The following industry guidance, cited in Pankow and Cherry, 1996, is notable:

Routine disposal practices Vapor Degreasing Sludge that Contains Chlorinated Solvents (1964):

Any procedure for disposal depends on local, state and federal regulations. In the absence of any clearly defined ordinances, the sludge is usually poured on dry ground well away from buildings, and the solvents are allowed to evaporate. If the sludge is free flowing, it is placed in shallow open containers and allowed to evaporate before the solids are dumped on the ground. [American Society of Metals, Metals Handbook: Heat Treating, 8th Edition, Volume 2. Metals Park, Ohio]

Chlorinated Solvent Disposal (1972):

Waste mixtures should not be discharged into drains or sewers where there is a danger that the vapor may be ignited. In cases such as these, the waste should be removed to a safe location (away from inhabited areas, highways, buildings, or combustible structures) and poured onto dry sand, earth, or ashes, then cautiously ignited. Burning of chlorinated hydrocarbon wastes should be done only when permitted by controlling authorities and then under constant supervision. In other instances, the chlorinated hydrocarbon waste may be placed in an isolated area as before and simply allow the liquid to evaporate. [Chemical Hazards Bulletin, American Insurance Association, C-86, March 1972. New York, NY. Pg. 42]

At electronics manufacturing, metals fabrication, and other industrial solvent release sites in the 1960's, 1970's and 1980's, improper disposal of still bottoms was often the cause of solvent contamination. Given the evidence for elevated concentrations of solvent stabilizers in still bottoms, stabilizers are likely to be present at these sites at elevated concentrations.

EXHIBIT 3.K

DECLARATION OF WAYNE C. TAM

I, Wayne C. Tam, hereby declare:

1. The following facts are within my personal knowledge.
2. I am a trustee of the Tam Family Trust dated May 16, 1991. The Tam Family Trust is the owner of the property located immediately adjacent to and north of West Chestnut Street in Alhambra, CA, between South Raymond Avenue and South Palm Avenue. I will refer to this property as 2015 West Chestnut Street.
3. I and my wife acquired the property located at 2015 West Chestnut Street from the Alhambra Redevelopment Agency in April 1980. The City of Alhambra ("the City") would only permit the sale and transfer of property from the Alhambra Redevelopment Agency if the property was sold as a vacant piece of land. Therefore, before the transaction, the City condemned or purchased the contiguous properties from the previous owners and demolished all of the buildings on those parcels before transferring the vacant land to me. These steps included removing the demolished structures and debris, including the concrete slabs, foundations, wood and metal debris. After the demolition was completed, the contractors for the Alhambra Redevelopment Agency regraded the site. At the time the sale was completed and the property transferred to me and my wife, the land was unpaved and roughly graded.
4. Another condition of the sales agreement was that we were required to construct on the vacant property four light industrial buildings. The buildings we constructed in compliance with this requirement are the existing Buildings 1 through 4 as shown on the attached figure.

5. When the construction of Buildings 1 through 4 was completed in 1981, around 95% of the land was covered by concrete pavement or concrete buildings constructed on concrete slabs. The only unpaved areas were street frontage strips along West Chestnut, South Palm, South Raymond and two 3' narrow strips along the southern sides of Buildings 3 and 4 inside the parking lot. The unpaved areas were all landscaped with a grass lawn and/or plantings.
6. After the construction was completed, the buildings were leased out to different companies, including Ortel Corporation beginning in 1981. In 1981, Ortel leased only a portion of Building 1, but expanded into Building 2 gradually between 1982 to 1986. By 1986 or earlier, Ortel was leasing all of Building 2. To my knowledge, none of our other tenants on this property have been industrial businesses using chemicals.

I certify under penalty of perjury under the laws of the State of California that the foregoing is true and correct.

Dated: 22ND day of OCTOBER, 2010
in ALHAMBRA, California



Wayne C. Yam

EXHIBIT 3.N