HALOGENATED HYDROCARBON SOLVENTS

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Received July 16, 1936

Halogenated hydrocarbons, especially the chlorinated derivatives, have been finding extensive use in degreasing, dewaxing, dry cleaning, extraction, and similar operations. A number of patents have been issued on uses in these fields. For instance, Farrington (36) has covered non-inflammable mixtures of petroleum naphthas with carbon tetrachloride as cleaning fluids. Another patent (60) deals with cleaning fluids containing less than 37.5 to 40.5 per cent of ethylene dichloride and more than 59.8 to 62.5 per cent of carbon tetrachloride. Other dry-cleaning fluids covered are aliphatic saturated unsymmetrical polychloro substitution products (67), a mixture (14) containing 1 per cent of tetrachloroethane, 3 to 5 per cent of dichloroethyl ether, 6 to 4 per cent of carbon tetrachloride, and 90 per cent of Stoddard solvent, and a mixture (71) containing 4 per cent of tertiary-amyl alcohol, 16 per cent of ligroin, and 80 per cent of carbon tetrachloride. An interesting patent (68) describes a non-inflammable solvent mixture comprising a non-inflammable solvent and an inflammable substance of the same volatility as the non-inflammable solvent, so that no appreciable fractionation occurs when the solvent is evaporated. A paint and varnish remover has been described which contains a mixture of solvents including a volatile inflammable solvent and a volatile non-inflammable solvent, composed of trichloroethylene, the proportion of trichloroethylene being sufficient to suppress the inflammability of the former so that the composition does not ignite, together with some wax.

Dry-cleaning fluids containing 0.1 to 3 per cent of a "lusterizing" agent such as chlorinated naphthalene in chlorinated solvents have been disclosed (67a). Another cleaning solvent contains a naphtha of 290–325°F. boiling range with acetylene tetrachloride to yield a non-inflammable composition (68b). A mixture of naphtha having a boiling range of 160–230°F. with 60 to 65 parts of carbon tetrachloride also has been recently proposed (68a). Still another cleaning solvent comprises 10 to 20 per cent of a petroleum distillate boiling at 70–134°C., 20 to 88 per cent of carbon tetrachloride, and 2 to 70 per cent of tetrachloroethylene (26a). This mixture is claimed to be non-explosive in all boiling ranges.

In one patent (66a) a flame-resistant solvent is produced by intensively chlorinating a mixture of gaseous hydrocarbons, removing a fraction boiling at 60–310°F., and blending it with 5 to 60 per cent of a petroleum fraction having distillation characteristics similar to that of the selected fraction.

PREPARATION

A large number of methods are available for the preparation of halogenated solvents. At the present time chlorinated hydrocarbons appear to have the greatest commercial significance, and most of the literature deals with these derivatives. Carbon tetrachloride is generally prepared by the interaction of carbon disulfide with sulfur dichloride (1, 38) in the presence of iron, while chloroform is obtained by treating carbon tetrachloride with steam in the presence of iron. This is peculiar in view of the fact that cheap methane is available and that all of its chlorine derivatives can be separated by fractionation. Very likely the reason is that the present process does not involve much loss of chlorine as hydrogen chloride. A number of patents have been issued covering improved methods of direct chlorination of saturated hydrocarbons (24, 25, 32, 41, 42, 56). Possibly some commercial processes will be developed wherein the hydrogen chloride may be utilized in other syntheses. Methylene chloride has been prepared by the chlorination of methyl chloride (43).

Photochemical chlorination of methane is reported to give up to 29 per cent of chlorine going to methyl chloride (80 per cent of the total chlorine being utilized), the methane to chlorine ratio varying from 15:1 to 19:1. The energy utilization, however, is low (57a). The removal of chlorinated products, followed by recycling of unreacted hydrocarbons, has likewise been disclosed in the literature (43a). Continuous removal of hydrogen chloride is provided for where the substance is detrimental (42a). In another modification, the chlorinated products are removed and the remainder mixed with fresh feed and chlorinated (44a). The hydrogen chloride from the reaction products may also be treated directly with methanol in the presence of a catalyst to produce methyl chloride (41a).

The two-carbon atom derivatives are mostly derived commercially from ethylene and acetylene. According to Curme (23), the best way of preparing ethylene dichloride is to react the liquid chlorine and ethylene at the vapor pressure of chlorine. It is also obtained as a by-product in the production of ethylene glycol. Other methods for producing this product have also been reported (11, 35, 39, 53, 54, 69). According to Maier (53) the chlorination of ethylene at 25°C. produces 70 per cent of trichloroethane, 15 per cent of ethylene dichloride, 5 per cent of tetrachloroethane, and 10 per cent of higher chlorinated products. Ethylene reacts readily with hydrogen chloride to produce ethyl chloride (12, 54, 59, 70, 72, 73, 74). This product may be further chlorinated. The treatment of alcohol with hydrogen chloride will also produce ethyl chloride (44).

Acetylene is a valuable raw material for the preparation of chloro derivatives. By chlorination it is converted to tetrachloroethane (54), which yields *sym*-dichloroethylene on treatment with iron or zinc, or trichloroethylene on treatment with slaked lime (7, 64). The chlorination of trichloroethylene gives pentachloroethane, which on treatment with slaked lime gives perchloroethylene. Trichloroethane may also be prepared by the chlorination of vinyl chloride (45, 48) or by chlorinating acetylene in the presence of hydrogen chloride (46). In the latter case a 90 to 98 per cent yield of product is obtained having the following composition: 10 to 15 per cent of dichloroethylene, 60 to 70 per cent of trichloroethane, 10 to 25 per cent of acetylene tetrachloride, 0 to 5 per cent of higher products. Dichloroethylene may also be prepared by direct chlorination of acetylene (47, 57), and by treating acetylene with tetrachloroethane in the presence of a hydrogenation catalyst at 350°C. (19a). Ethylidene chloride has been produced by treating vinyl chloride with hydrogen chloride (26).

In one patent (27a) chlorine is reacted with a saturated aliphatic hydrocarbon of three to five carbon atoms to form a mixture of saturated chlorohydrocarbons, hydrogen chloride, and olefins. The latter two products are then reacted at a temperature below 200°C. The formation of dichloroethylene derivatives is claimed when chlorine is reacted with a mixture of trichloro- and tetrachloro-propanes and -butanes (70a). Cracked gases have been likewise chlorinated in two stages (23d), the more reactive hydrocarbons (unsaturates) being reacted in the first stage. Substitution of halogen in paraffin hydrocarbons, and addition of halogen to olefins has been effected simultaneously in a mixture of hydrocarbons by the action of free halogen in the absence of oxygen in the dark at below 100°C. (64a).

Isopropyl chloride (16, 17), *n*-propyl chloride (50), propylene dichloride (30), butyl chlorides, (22, 61), and chlorinated acid extract (34) have also been prepared as raw materials for this purpose. Commercial chlorination of pentanes (9, 10, 20) has made available a large supply of monochloro derivatives and by-product dichloropentanes. According to some investigators (72a), chlorination of pentane, hexane, and heptane (unlike the case of aromatics) is not accelerated by antimony pentachloride.

Cyclic chlorinated hydrocarbons are used as solvents to a certain extent in industry. Direct chlorination is usually resorted to in the presence of catalysts, such as in presence of a copper catalyst at 300°C. (49, 59a), in the vapor phase at high temperature with aluminum, copper, iron, and cerium (55a, 72b), also with sulfur, antimony chloride, and lead (28a). Monochloro aromatic hydrocarbons have also been further chlorinated to

TABLE 1

Experimental data

FRACTION °F.	PER CENT OF TOTAL	SPECIFIC GRAVITY	COLOR AFTER NEUTRALIZATION	INSTABILITY[j]		K.B. SOLVENT POWER		BURNING TEST
				After neutralization	After hydrolysis	After neutralization	After hydrolysis	
Charge—hydro solvent[a]								
158–230	15	0.8270	Water white					Yes[f]
230–284	22	0.8808	Water white					Yes
284–338	30.6	0.9643	Green		385	76.7	77.4	No
338–345	23	1.0846	Brown					No
Residue	9.4		Black					
Charge—stabilizer bottoms[b]								
104–230	3.7							Yes
230–272	17.3	0.916						Yes
272–292	18.7	0.985						Barely
292–320	17.3	1.056				76.4[c]	75.4[c]	No
320–374	31.1	1.167		206[d]				No
Charge—stabilizer bottoms[e]								
To 230	0							
230–278	6.7							Yes
278–320	37.3	1.0137		496	460	73.9		No
320–374	42.7	1.0827			520			No
374–410	12.0	1.1626						No
Residue and loss	1.3							
Charge—commercial amyl chlorides[g]								
To 230	58.6	0.8725	Colorless					Yes
230–266	2.6		Colorless					Yes
266–320	22.8	1.077	Colorless	630	565	82		No
320–370	11.1	1.147	Colorless	430	423			No
370–410	2.9	1.296	Colorless					No
Residue	2.0							
Charge—Edeleanu extract[h]								
300–350[i]			Colored	65				No

(a) B.P. 176–212°F. K.B. value = 57.9. Chlorinated to 20 per cent Cl at 185°F.

(b) Contains about 67 per cent pentanes and pentenes, 26 per cent hexanes and hexenes, and 7 per cent boiling in heptane range, total unsaturates being about 35 per cent. Chlorinated to 38.5 per cent (sp. gr. 1.090).

(c) For combined fractions 272–374°F.

(d) For combined fractions 375–450°F.

(e) Same as (b) treated with 20 per cent by volume of concentrated sulfuric acid.

(f) "Yes" in burning test means that sample will flash when lighted match is passed over surface on glass plate.

(g) Mixture of commercial amyl monochlorides. Chlorinated at 180°F. for 4½ hours in glass to 0.8715–0.9835 sp. gr.

(h) B.P. 340–430°F. Chlorinated at 60–70°F. to 39 per cent Cl.

(i) At 2 mm.

(j) Ten cc. refluxed with 25 cc. water for 2 hrs. and titrated with 0.1 *N* caustic.

produce higher boiling products (32a, 71a). In the preparation of chlorotoluene, it has been pointed out (48a) that direct chlorination at 250–600°C. without catalysts results in substitution entirely in the side chain, whereas catalysts direct the reaction towards nuclear chlorination.

Experimental data on the chlorination of various petroleum products are presented in table 1. In order to obtain the best yields, it has been found desirable to chlorinate in glass vessels in the absence of iron with good dispersion of the chlorine and hydrocarbon. A reflux condenser may be attached to avoid evaporation of the lighter fractions. Very good yields of the lower boiling chlorides were obtained, especially in view of the fact that the low-boiling inflammable fractions may be rechlorinated without difficulty. In the case of sulfur dioxide extract, the presence of the heavier fraction produced considerable coking, so that only the light fraction (50 per cent) was found to give satisfactory results.

The lower boiling gasoline polychlorides are satisfactory for certain types of outside paints and preparations where non-ignitability is of prime importance. They also have possibilities in dewaxing and other uses.

With recent advances in chlorination technique (21, 51, 65) there is a possibility of improving the stability of chlorinated higher hydrocarbons by selective direction of the chlorine with special solvents, peroxides, etc.

Fluorinated hydrocarbons (13) and similar aliphatic products have also been described (3, 4, 5, 8, 15, 18, 31, 37, 38a, 52, 58). They are generally prepared by reacting a chlorinated hydrocarbon with antimony trifluoride, such as by the reaction:

$$3CCl_4 + 2SbF_3 = 3CCl_2F_2 + 2SbCl_3$$

SOLVENCY

The solvent power of most paint and varnish solvents is expressed as per cent of benzene (benzol) solvency by the kauri butanol test (2, 11a). This test, of course, determines the solvent action on gum kauri, and although it has proved to be a good indicator for general purposes, its merit may not be as great in the dry-cleaning and other industries.

Generally, it may be stated that halogenation improves the kauri butanol value of hydrocarbons, although there appears to be an exception in the case of fluoro aromatics. The effect of halogenation on aromatic hydrocarbons is shown by the following data:

Compound	*K. B. solvent power per cent*
Benzene	100.0
Bromobenzene	128.8
Chlorobenzene	115.2
Fluorobenzene	93.0

Chlorination of aromatics and their homologs raises the kauri butanol solvent power, but not to as high an extent as in the case of the aliphatics. Some results obtained are as follows:

Compound	*K. B. solvent power per cent*
Benzene	100.0
Chlorobenzene	115.2
Toluene	93.8
o-Chlorotoluene	108.8

In the case of the saturated aliphatic hydrocarbons having two to eight carbon atoms per molecule, the effect of chlorination seems to be fairly definite (within a few kauri numbers) and might be given as follows:

No. of Cl atoms per molecule	*K. B. solvent power per cent*
0	25
1	60
2	82
3	100 (approx.)

Methane, however, is an exception. In this case chlorination raises the solvency markedly, until all of the hydrogen is replaced with chlorine, when a sudden drop in solvency results:

Compound	*K. B. solvent power per cent*
Dichloromethane	116.0
Chloroform	156.7
Carbon tetrachloride	92.1

As shown in table 1, non-inflammable chlorinated petroleum hydrocarbons of 75 kauri butanol solvent power may be prepared in high yields. It has been found that refluxing with caustic generally improves the kauri butanol solvent power (probably owing to the formation of hydroxyl groups), while ordinary steam distillation has a tendency to decrease the kauri butanol value somewhat, possibly because of dechlorination.

STABILITY

For many purposes, e.g., preparation of metal paints, dry-cleaning solvents, etc., it is essential that the solvent employed should not produce excessive acidity. On the other hand, in many uses, notably in the outside paint industry, this element is not of such marked importance, since the small amount of acidity produced would not be very injurious to the concrete, wood, brick, and other substantially inert material coated, provided the proper containers are used.

The test for instability employed herein consists in refluxing 10 cc. of the solvent with 25 cc. of water for 2 hours, and titrating the free acidity with 0.1 *N* caustic. Although it is not exactly comparative, it is sufficiently satisfactory to give a good indication of the relative instability of the product in the presence of water. Iron generally greatly accelerates the decomposition of moist chlorinated products, while oil tends to decrease it in most cases.

As a general rule, the bromides are less stable than the chlorides, while the fluorides are considered more stable.

The tests reported in table 2 indicate that the chlorine attached to a primary aliphatic carbon atom is much more stable than that on the secondary, which is in turn more stable than that on the tertiary. That is why the methyl and ethyl derivatives, such as carbon tetrachloride and ethylene dichloride, are relatively so much more stable than other aliphatic chloro derivatives. The tendency in ordinary chlorination is to form the least stable chloride if the groups are available. In the case of the higher homologs, adjacent chlorine atoms, such as those produced by the usual chlorination of unsaturates, produces a very unstable molecule which tends to split off hydrogen chloride to give a more stable unsaturated derivative. The reaction may be carried out by steam distillation of the compound. Refluxing with caustic often effects this, although the usual tendency is to produce a hydroxyl group. Propylene chloride possesses a high degree of stability in spite of the presence of a secondary carbon atom.

In the case of carbon tetrachloride it must be remembered that, in the presence of iron, iron oxide is deposited according to the reaction:

$$2CCl_4 + 2Fe + H_2O = 2CHCl_3 + FeCl_2 + FeO$$

This is in addition to the true hydrolysis, which is apparently the main reaction undergone by most of the higher homologs:

$$C_2H_4Cl_2 + 2H_2O = C_2H_4(OH)_2 + 2HCl$$

The rate of hydrolysis appears to increase for these compounds in the following order: trichloroethylene, carbon tetrachloride, ethylene dichloride.

According to Dickinson and Leermakers (23b), photoöxidation of tetrachloroethylene in carbon tetrachloride is strongly inhibited by oxygen. In the presence of both chlorine and oxygen, photosensitized oxidation to trichloroacetyl chloride, and to some extent to phosgene, occurs.

The chlorinated aromatics, i.e., those which have the chlorine attached directly to the nucleus, are considered to be very stable compounds, while the naphthenic chlorides appear to be exceptionally unstable.

A large number of proposals have been made for inhibiting the decom-

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Data on halogen

COMPOUND	FORMULA	BOILING POINT		FREEZING POINT
		°*C.*	°*F.*	°*F.*
Methyl chloride	CH_3Cl	−23.7	−10.7	−143.
Dichloromethane (methylene dichloride)	CH_2Cl_2	39.8	103.5	−143.
Chloroform	$CHCl_3$	61.2	142.2	−81.7
Carbon tetrachloride	CCl_4	76.0	168.8	−9.4
Ethyl chloride	C_2H_5Cl	12.5	54.5	−217.7
Dichloroethylene	$CHCl:CHCl$	48.4	119.1	−58
Dichloroethylene	$CHCl:CHCl$	60.3	140.5	−112.9
Dichloroethylene[b]		55.0	131.0	−112.9
Ethylene dichloride (dichloroethane)	$CH_2Cl \cdot CH_2Cl$	83.7	182.7	−31.5
Ethylidene chloride	$CH_3 \cdot CHCl_2$	58–60		
Chlorasol	75% $C_2H_4Cl_2$; 25% CCl_4	77–83	171–182	
Ethylene dibromide	$C_2H_4Br_2$	131	265	47
Trichloroethylene	$CHCl:CCl_2$	86.7	188.0	−126.4
Trichloroethane (beta)	$CHCl \cdot CCl_2$	113.5	236.3	−34.1
Triasol		82	180	
Tetrachloroethane (*sym*)[d]	$CHCl_2 \cdot CHCl_2$	146.3	295.3	−46.8
Tetrachloroethylene	$CCl_2:CCl_2$	118–122	244.4–251.6	−8.3
Perchloroethylene	$CCl_2:CCl_2$	120.8	249.5	−8.3
Pentachloroethane	$CHCl_2 \cdot CCl_3$	159.0	318.2	−7.6
Hexachloroethane	$CCl_3 \cdot CCl_3$	185[s]	365[s]	83.5
n-Propyl chloride	C_3H_7Cl	46.5	115.5	−189
Propylene dichloride	$CH_3CHCl \cdot CH_2Cl$	95.9	204.6	<−112
n-Butyl chloride	C_4H_9Cl	78	173	−190
sec-Butyl chloride	C_4H_9Cl	68	154	
tert-Butyl chloride	$(CH_3)_2CClCH_3$	51	124	19
n-Butylidene chloride	$CH_3CH_2CH_2CHCl_2$			
sec-Amyl chloride	$C_5H_{11}Cl$	105	221	
tert-Amyl chloride	$C_5H_{11}Cl$	85.7	186	−99
Amyl dichlorides[e]	$C_5H_{10}Cl_2$		270–320	
Amyl dichlorides[f]	$C_5H_{10}Cl_2$		275–320	
Amyl trichlorides[e]	$C_5H_9Cl_3$		320–375	
Amyl trichlorides[f]	$C_5H_9Cl_3$		320–375	
Chlorinated hydrocarbon[f]			375–450	
Chlorinated hydrocarbon[g]				
sec-Hexyl chloride	$C_6H_{13}Cl$			
Cyclohexyl chloride	$C_6H_{11}Cl$	142.5	288.5	
Chlorinated SO_2 extract			300–350[i]	
Chlorobenzene (mono)	C_6H_5Cl	131.7	269	−49.4
o-Dichlorobenzene	$C_6H_4Cl_2$	180.3	357	2
p-Dichlorobenzene	$C_6H_4Cl_2$	173.0	343.4	
Trichlorobenzene[u]	$C_6H_3Cl_3$	213–217	415.4–423.6	46.4–51.8
o-Chlorotoluene	$ClC_6H_4CH_3$	159.2	319	−33
Bromobenzene	C_6H_5Br	155.9	312	−23
Fluorobenzene	C_6H_5F	84.6	184	−39

(a) At 12.5°/40°C. (b) Mixture of isomers b.ps. 48°C. and 60°C. (c) At 15°/40°C. (d) Dis
stabilizer bottoms. (g) From chlorination of hydrogenated solvent b.p. 176–212°F. (h) Burns
14°C. (m) At 25°C. (n) Gasoline = 25; 176–212°F. hydro solvent = 58; benzene = 100. (p) At
4°C. (u) 85 to 90 per cent of 1,2,4- and 10 to 15 per cent of 1,2,3-trichlorobenzene. (v) Inflamma
with 25 cc. of water for 2 hrs. and titrated with 0.1 *N* caustic.

GRAVITY	(CC.) FLASH	KAURI BUTANOL SOLVENT POWER[n]	RELATIVE TOXICITY[k]	INSTABILITY (cc. N/10 NaOH PER 100 cc.)[x]		VAPOR DENSITY AT 15°C.	LATENT HEAT OF VAPORIZATION	SPECIFIC HEAT (LIQUID) AT 20°C.	FLAMMABILITY
				Distilled	Redistilled over NaOH				
lbs. per gallon	°*F.*					*lbs. per cubic foot*	*B.T.U. per lb.*		
8.34[p]						0.154	184.3	0.382	Moderate
11.13		116.0				0.224	135.5	0.289 (15–40°C.)	Non[q]
12.52		156.7	2.2			0.315	106.4	0.254	Non
13.28	None	92.1	1.0			0.408	83.7	0.203 (25°C.)	Non[v]
7.69[r]						0.172	167.3	0.172	Flammable
10.49						0.230	132.6	0.270	Moderate
10.70						0.221	131.3	0.270	Moderate
10.7	57		1.7			0.241	127.8	0.270	Moderate
10.49	68[h]	82.1		4.7		0.211	139.2	0.301	Moderate[w]
					65				
11.2	None								
		105.6		99					
12.25	None	105.6	1.7	3.5		0.347	104.5	0.233 (18°C.)	Non
12.04		123.9				0.263	123.6	0.266	Non
11.1	84								
13.19	None		9.1			0.443	99.11	0.269	Non
13.4	None						90.3	0.21	Non
13.4	None		1.6			0.438	93.0	0.216	Non
14.1	None		6.2			0.535	78.5	0.266	Non
						0.393	83.5	0.174	Non
		67.1		5					
12.2	70	86.3		6		0.232	142	0.31	Moderate
		57.8							
		60.3							
				2000					
				266					
		62.4							
		57.6							
		82.0		630	565				
		73.9		496	460				
				430	423				
					520				
				206					
		77.4			385				
		57.9							
				2000					
9.2	84.4	115.2					139.8	0.31	Flammable
		115.5		2					
	152					0.317		0.30	Moderate
12.0									
		108.8							
		128.8							
		93.0							

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per cent sulfur. (e) Commercial mixture of isomers. (f) From chlorination of acid-treated iculty. (i) At 2 mm. (j) At 16°/15°C. (k) Gasoline = 2.3; carbon disulfide = 24.3. (l) At . (q) Will not burn even on boiling in open crucible. (r) At 0°C. (s) Sublimes. (t) At 54°/ mits 9.7 to 12.8 per cent. (w) Inflammability limits 3 to 14 per cent. (x) Ten cc. refluxed position of chlorinated hydrocarbons. Most of the methods involve the addition of basic or unstable materials such as amines (6, 23c), gums (27), dyes (28), hydrocarbons (29, 62), etc., but they generally involve the neutralization or addition of the liberated hydrochloric acid rather than a true inhibition of the decomposition. Carlisle and Levine (19) state that trichloroethylene will not decompose in the light unless oxygen is present and recommend the addition of small amounts of anti-oxidants. However, in many cases, as in the dry-cleaning industry, the solvents must be recovered by distillation, involving the loss of inhibitor which is generally much higher boiling. The decomposition of methylene chloride was reported to be effected to a great extent by the amount of water present (19).

TABLE 3

Ignitable concentrations of mixed solvents

A	B	PER CENT A WHEN MIXTURE			
		Flashes and burns	Burns only	Ignites immediately	Will not ignite immediately
Acetylene tetrachloride	Ethyl acetate	20–40	50	60	70
Acetylene tetrachloride	Isopropyl alcohol	30	40–50	60	65
Carbon tetrachloride	Isopropyl alcohol			20	30
Carbon tetrachloride	Ethylene dichloride				25
Carbon tetrachloride	Ethyl acetate	30		40	50
Carbon tetrachloride	Benzene				70
Carbon tetrachloride	Gasoline				65
Methylene chloride	Ethylene dichloride				40
Trichloroethylene	Benzene				67
Trichloroethylene	Stoddard solvent				50
Trichloroethylene	Ethylene dichloride				65

It seems that the problem might be somewhat simplified if the more stable fluorides were made available at a low price. This, of course, applies only for cases requiring exceptionally stable solvents. Even in the case of these solvents, corrosion of copper and other metals has been encountered in "long-life" equipment such as refrigerator systems, although this is claimed to be minimized by the use of white oil and other special lubricants.

INFLAMMABILITY

For ordinary purposes, chlorinated solvents should be satisfactory if they do not ignite at room temperatures when momentarily exposed in thin films to flames. However, in many cases it is necessary to employ materials which will not ignite at elevated temperatures, and in such cases highly

TABLE 4

Flash points of mixed solvents

A	PER CENT A	B	PER CENT B	ORIGINAL FLASH POINT °F.
Trichloroethylene	80	Naphtha (72°)	20	180
Trichloroethylene	75	Benzine	25	180
Trichloroethylene	50	Kerosene	50	90
Trichloroethylene	67	Benzene (benzol)	33	187–90
		Turpentine	100	120
Trichloroethylene	75–83	Turpentine	17–25	192–5
Trichloroethylene	50	Stoddard solvent	50	None at 202
Trichloroethylene	75	Acetone	25	Below 34
Trichloroethylene	95	Acetone	5	70
Trichloroethylene	90	Acetone	10	45
Trichloroethylene	95	Isopropyl alcohol	5	75
Trichloroethylene	90	Isopropyl alcohol	10	65
Trichloroethylene	95	*sec*-Butyl alcohol	5	105
Trichloroethylene	90	*sec*-Butyl alcohol	10	95
Trichloroethylene	95	*tert*-Butyl alcohol	5	80
Trichloroethylene	90	*tert*-Butyl alcohol	10	70
Trichloroethylene	100			None
Ethylene dichloride	100			Below 60
Ethylene dichloride	90	Chloroform	10	65
Ethylene dichloride	70	Chloroform	30	90
Ethylene dichloride	60	Chloroform	40	None
Ethylene dichloride	90	Carbon tetrachloride	10	70
Ethylene dichloride	80	Carbon tetrachloride	20	80
Ethylene dichloride	70	Carbon tetrachloride	30	None
Ethylene dichloride	90	Trichloroethylene	10	55
Ethylene dichloride	60	Trichloroethylene	40	65
Ethylene dichloride	40	Trichloroethylene	60	95
Ethylene dichloride	80	Methylene chloride	20	60
Ethylene dichloride	65	Methylene chloride	35	70
Ethylene dichloride	60	Methylene chloride	40	None
Dichloroethylene	100			50
Chloroform	100			None
Carbon tetrachloride	100			None
Carbon tetrachloride	60	Acetone	40	Below 32
Carbon tetrachloride	70	Acetone	30	Below 32
Carbon tetrachloride	80	Acetone	20	57
Carbon tetrachloride	20	Toluene	80	57
Carbon tetrachloride	30	Toluene	70	74
Carbon tetrachloride	40	Toluene	60	Above 86

chlorinated products are required. This, of course, is not the only factor, since vapor pressure (boiling point), thermal stability, and other factors also enter. For instance, Ellis (33) has shown that solid chlorinated derivatives dissolved even in large quantities in inflammable solvents will not appreciably reduce the inflammability of the latter.

In the case of the aliphatics, the amount of chlorine necessary to give a non-flashing product at ordinary temperature decreases with increase in boiling point. A rough approximation of the minimum requirement for non-inflammability at ordinary temperatures may be obtained from the following table:

TABLE 5

Toxicity of chlorinated hydrocarbons

CHLORINATED HYDROCARBON	FORMULA	RELATIVE TOXICITY (CCl_4 = 1)
Carbon tetrachloride	CCl_4	1.0
Perchloroethylene	C_2Cl_4	1.6
Trichloroethylene	C_2HCl_3	1.7
Dichloroethylene	$C_2H_2Cl_2$	1.7
Chloroform	$CHCl_3$	2.2
Pentachloroethane	C_2HCl_5	6.2
Tetrachloroethane	$C_2H_2Cl_4$	9.1

TABLE 6

Toxicity of chlorinated hydrocarbons

CHLORINATED HYDROCARBON	FORMULA	RELATIVE TOXICITY
Ethyl chloride	C_2H_5Cl	1.0
Carbon tetrachloride	CCl_4	3.0
Trichloroethane	CH_3CCl_3	3.5
Ethylidene dichloride	CH_3CHCl_2	4.3
Dichloromethane	CH_2Cl_2	4.3
Trichloroethylene	$CHCl{:}CCl_2$	5.6
Dichloroethylene	$CHCl{:}CHCl$	6.0
Chloroform	$CHCl_3$	7.0
Dichloroethane	CH_2ClCH_2Cl	8.0
Tetrachloroethylene	$CCl_2{:}CCl_2$	9.3
β-Trichloroethane	$CH_2Cl \cdot CHCl_2$	14.0
Tetrachloroethane (*sym*)	$CHCl_2 \cdot CHCl_2$	16.0
Pentachloroethane	$CHCl_2 \cdot CCl_3$	18.7

Series chlorinated	*Per cent chlorine which must be substantially exceeded to prevent flashing*
Methane	90
Ethane	70
Pentane	53

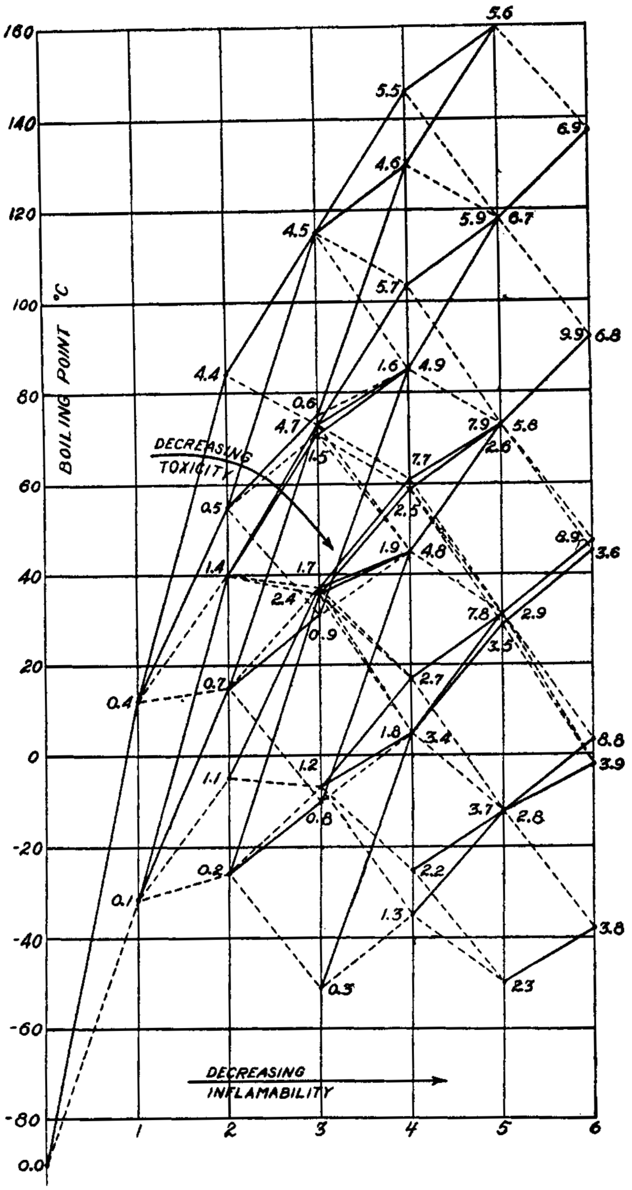

FIG. 1. Properties of fluoro-chlorinated hydrocarbons. 0 = CH_3; 1 = CH_2F; 2 = CHF_2; 3 = CF_3; 4 = CH_2Cl; 5 = $CHCl_2$; 6 = CCl_3; 7 = $CHClF$; 8 = $CClF_2$; 9 = CCl_2F.

Table 3 lists the ignitable concentrations of mixed solvents, while table 4 gives the flash points of such mixtures. It must be borne in mind that the inflammability of a mixture may vary with the amount and rate of solvent evaporated, depending on the vapor pressures of the components and other factors (66, 68).

Because of their higher boiling points, the butyl and amyl polychlorides offer possibilities in the solvent field, especially since a lower amount of chlorine is necessary to produce non-inflammable properties. Where high stability is not required, they should be available at a cheap price.

TOXICITY

One important property of these materials is toxicity. There does not seem to be any definite correlation between structure and toxicity, the relative toxicities being given by Henderson and Haggard as shown in table 5 (40). This relationship is somewhat modified by Lazarew (52a), who gives the values shown in table 6.

The fluorinated compounds possess the advantage of physiological inertness, which should make them well fitted for solvent uses from this viewpoint.

Figure 1, taken from U. S. patent 1,968,050 (55), illustrates the relative toxicity of chlorides and fluorides in two-carbon atom molecules. The base line indicates the number of atoms of halogen per molecule. By means of the key given, it is possible to locate the effect of the various substituents. For instance, compound 0.1 is CH_3CH_2F, compound 2.9 is CHF_2CCl_2F, and compound 2.2 is CHF_2CHF_2. The dashed lines indicate fluorine substitutions, and the solid lines indicate chlorine substitutions. It will be seen that the substitution of fluorine for chlorine greatly reduces the toxicity and also reduces the boiling point.

The aromatic chlorinated derivatives are generally considered quite toxic. These might also be improved by fluorination.

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