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An Overview of Fluorocarbons

Introduction

Currently, chlorofluorocarbons are garnering a lot of attention around the world. Chlorofluorocarbons are used in many of our products and when we look at the future of chlorofluorocarbons in the world, and in Japan, we can foresee that their use will be strictly limited or eliminated all together.

Whatever the case, Three Bond Co., Ltd. is obligated to provide our customers with products that have the same functionality as chlorofluorocarbons.

Three Bond Co,. Ltd. has been working night and day in search of alternatives to chlorofluorocarbons. In the future, products that do not contain any chlorofluorocarbons will replace products that now contain chlorofluorocarbons. To ensure these products reach our customers as smoothly as possible, it is important that they have a good understanding of the issues surrounding chlorofluorocarbons.

Contents

1. What is a fluorocarbon?

Fluorocarbon is a generic name for a compounds that contains between one and three carbon atoms with fluorine, chlorine, bromine, or hydrogen. When the carbon is combined with chlorine or fluorine it is called a chlorofluorocarbon (CFC) and when it is combined with hydrogen it is called a hydrochlorofluorocarbon (HCFC).

2. Properties of fluorocarbons

Fluorocarbons have the following advantages,

(1) Stabilize when heated

(2) Nonflammable

(3) Metal corrosion is minimal

(4) Excellent oil-solubility

(5) Great electro-insulation

(6) Low level of toxicity.

These days, large quantities of fluorocarbons are used as refrigerants, abstergent aerosol propellants and plastic blowing agent.

3. Types of fluorocarbons

The ability of fluorocarbons to destroy the ozone layer depends on their molecular structure. The chlorine and bromine in chlorofluorocarbon molecules (those that contain bromine are called halons) destroy the ozone layer. Fluorocarbons are classified into the following three types depending on their molecular structure.

Type I .... Ozone depleters (Fluorocarbons that contain chlorine and bromine and no hydrogen. Fluorocarbons with this molecular structure do the most damage to the ozone layer.) = CFC

Type II ...... Biodegradable (This type of fluorocarbon contains hydrogen that is easily broken down in the troposphere, before it has a chance to reach the stratosphere, thereby limiting its ability to deplete the ozone layer.) = HCFC

Type III ..... Ozone safe (This type of fluorocarbon does not damage the ozone because it does not contain chlorine nor bromine.) = HFC

Typical chlorofluorocarbons include CFC11, CFC12, which are gaseous at room temperature, and CFC113, which is a liquid at room temperature and often used as a cleaner. (Refer to Table 1)

Table 1. Structure of fluorocarbon and the application

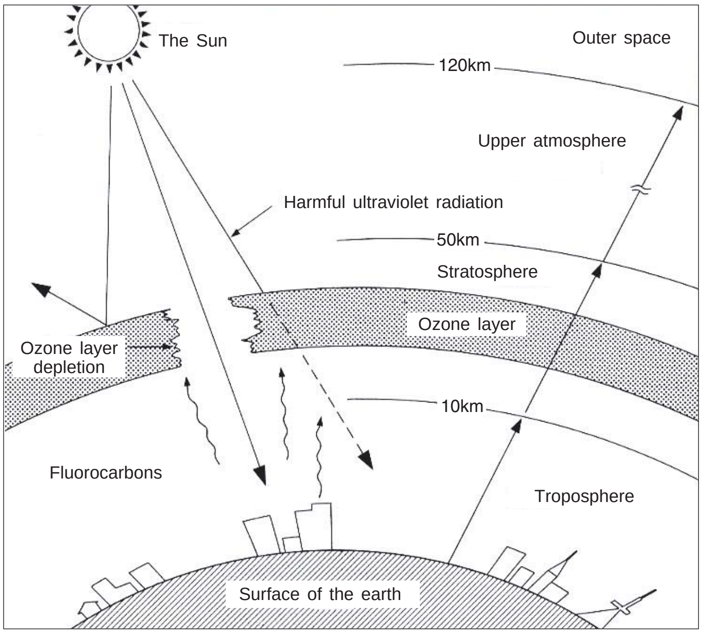
	Fluorocarbon number	Molecular formula	Classification based on ability to deplete the ozone	Applications
Methane system	11	CCl_3F	I	Propellants, Refrigerants, Blowing agents, Cleaners
	12	CCl_2F_2	I	Propellants, Refrigerants, Blowing agents
	13	$CClF_3$	I	
	14	CF_4	III	Dry etching agents
	21	$CHCl_2F$	II	
	22	$CHClF_2$	II	RefrigerantsÅAWorking fluids
	23	CHF_3	III	Working fluids, Dry etching agents
Ethane system	112	$CCl_2F\text{-}CCl_2F$	I	Cleaners
	113	$CClF_2\text{-}CCl_2F$	I	Cleaners and working fluids
	114	$CClF_2\text{-}CClF_2$	I	
	115	$CClF_2\text{-}CF_3$	I	
	116	$CF_3\text{-}CF_3$	III	
	142b	$CH_3\text{-}CClF_2$	II	
	152a	$CH_3\text{-}CHF_2$	III	Glass Surface preparation

4. Mechanism of ozone layer depletion

Ozone is a gas that is widely distributed from ground level all the way up through the upper atmosphere. It is highly concentrated in the ozone layer, which is in the stratosphere at an altitude of about 30km.

The ozone layer absorbs shortwave UV rays (UB-V), those are deleterious to living organisms, that pours down from the sun and prevents them from reaching ground.

What we call "ozone layer depletion" is a decrease in the concentration of ozone in this layer. The mechanism of depletion is as follows; chlorofluorocarbons consumed on ground rise up to the stratosphere, they are irradiated by ultraviolet rays, they react with the ozone and breaks it down into oxygen. In this case, chlorofluorocarbons do not react with ozone directly, the chlorine atom that is generated when a chlorofluorocarbon breaks down reacts with the ozone. Moreover, it is said that this single chlorine atom can destroy around 100,000 ozone atoms, and its great destructive ability is one of the causes of ozone layer depletion.



Stratospheric ozone layer. The ozone layer is over 10km thick, however, if it were in the same atmospheric pressure that we experience on the ground it would only be 3mm thick.

Figure 1. Mechanism of depletion of the ozone layer <I>

$$\mathrm{CFC} \xrightarrow{\text{Ultraviolet radiation}} \mathrm{Cl}$$

$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$

$$\mathrm{ClO + O \longrightarrow Cl + O_2}$$

$$\mathrm{O_3 + O \xrightarrow{Cl} 2O_2}$$

Figure 2. Mechanism of depletion of the ozone layer <II>

5. Why is chlorine used with fluorocarbons?

If chlorine is so detrimental to the ozone layer then why do we continue to use it in fluorocarbon molecules. There are two major reasons for this. One reason is that introduction of chlorine into fluorocarbons raises the boiling point making it easy to use. Another reason is that the fluorocarbons' affinity to oil improves tremendously when chlorine is present in the molecule.

Figure 3 shows the changes that can be seen in the boiling point when the hydrogen atoms in the methane are substituted one by one with halogen. As you can see, there is not much change seen in its boiling point when fluorine is introduced into the methane. The boiling point of difluoromethane rises slightly, however, this is because the molecule becomes asymmetrical and an attraction of the dipoles occurs at the molecular level. This causes the boiling point of tetrafluoromethane to fall again, and it approaches the boiling point of methane itself. In comparison, you can see that when chlorine and bromine are introduced into the methane, the boiling point rises sharply. In other words, as shown in the figure, fluoromethane is hard ?to-use as a gas because of its low boiling point, but chlorofluoromethane is a gas that is easy to use because of its high boiling point (CFC11, CFC12 , HCFC22).

It is well known that the chlorocarbons have higher lipophilicity than fluorocarbons do. For instance, some typical chlorinate solvents include triethane, tetrachloroethane and trichloroethane, which are extremely strong. Comparatively CFC113, a chlorofluorocarbon, is appreciated because it is a solvent mild enough not to damage plastic. However, fluorocarbon that do not contain any chlorine at all are sometimes hard to use because they do not blend well with some organic matter, such as oil.

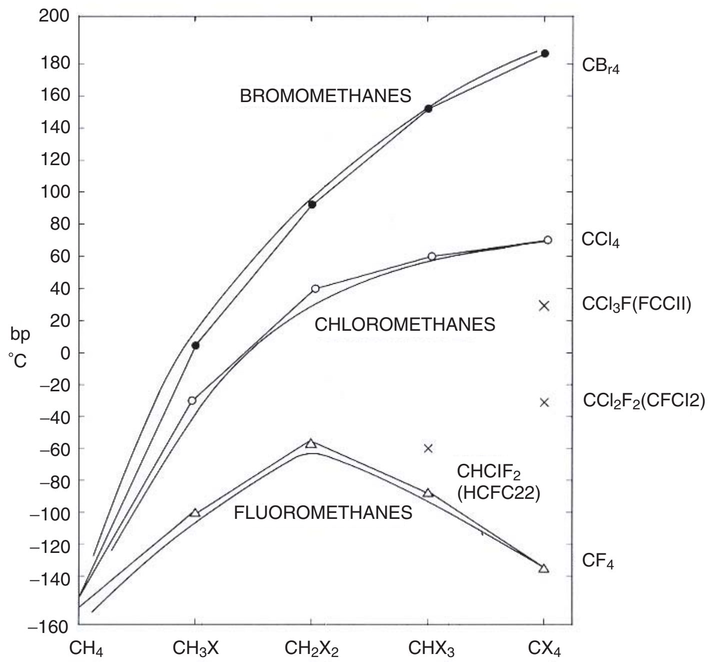


Figure 3. Comparison of the boiling point of halomethanes

6. Restricted fluorocarbons

There are five kinds of fluorocarbons restricted by the Montreal Protocol. CFC11, CFC12, CFC113, CFC114 and CFC115, and you can see that all of them are Type I (ozone depleters) as shown in Table 1 in Chapter 3.

There are about 20 fluorocarbon manufacturers in the capitalist countries, including five Japanese manufacturers (identified below). The quantity of fluorocarbons produced in 1987, including production in the Soviet Union is estimated to total around one million tons of CFC11, CFC12 and CFC113. The U.S. accounts for 300,000 tons, Western Europe accounts for 400,000 tons, Japan accounts for 140,000 tons and the remainder is produced by Soviet Union, Eastern Europe, India, Brazil, and so on.

7. Meaning of the fluorocarbon number

In general, fluorocarbons are referred to by their the number, for example, CFC 11, CFC 12, and CFC 113.

These numbers are not just randomly assigned to fluorocarbons, they are identification numbers that show the structure of each fluorocarbon.

The following is an explanation of the meaning of the fluorocarbon number.

The fluorocarbon number

The ones digit............. The number of fluorines in the molecule.

The tens digit.............. The number of hydrogens in the molecule plus 1.

The hundreds digit ...... The number of carbons in the molecule minus 1.

This might not be enough to fully understand its molecular structure. Carbon (C) has four arms, so if carbon (C), hydrogen (H), and fluorine (F) are attached to the arms, there is still one arm available. The chlorines (Cl) will band with the remaining arm.

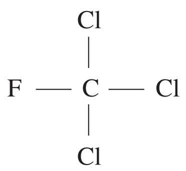
Example (1) CFC11

a) fluorine 1

b) hydrogen 0

c) carbon 1

Therefore, the structure is as shown below.



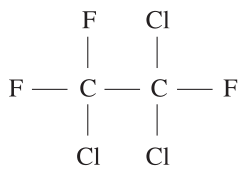
Example (2) CFC113

a) fluorine 3

b) hydrogen 0

c) carbon 2

Therefore, the structure is as shown below.



The molecular formula in Table 1 will help you deepen your understanding.

8. Fluorocarbon manufacturers in Japan

The following are the five fluorocarbon manufacturers in Japan.

1) Daikin Kogyo Co., Ltd.
2) Central Glass Co., Ltd.
3) Asahi Glass Company, Limited
4) Showa Denko K.K.
5) Du Pont-Mitsui Fluorochemicals Company, Ltd

9. Chlorofluorocarbon applications and the quantity produced.

In 1986 Japan produced about 140,000 tons of chlorofluorocarbons. The most common application was cleaning where CFC accounted for 38% of the total usage. The second most common application was for refrigerant, which is accounted for 31% of the usage. CFC11 and CFC12 are mainly used in air conditioners and CFC12 and CFC22 are mainly used in refrigerators. The fourth most common application was for aerosol propellant where CFC11 and CFC12 which accounted for 9% of the total usage.

10. Why do we need to completely abolish the use of chlorofluorocarbons by the end of this century in order to protect the ozone layer?

In 1960 around 150,000 tons of fluorocarbons were used, in 1987 that number jumped to 1,000,000 tons. Up to now we have used in excess of 15 million tons and it will take about ten years for all of these chlorofluorocarbons to reach the stratosphere as they are gradually pushed upwards by convection.

It is thought that only about 10% of the chlorofluorocarbons exhausted worldwide have reached the stratosphere. Depletion of the ozone layer has progressed considerably, even though 90% of the chlorofluorocarbons exhausted have not yet reached the stratosphere.

Therefore, many academics think that even if we completely abolish the use of CFCs today that it is still too late.

At the 1st Conference of the Parties (the contracting party of the Montreal Protocol that developes agreements for the regulation of CFCs) in Helsinki held on 2nd to 4th of May in 1989, it was agreed that the use of CFCs would be completely abolished by the end of this century.

11. Three Bond commodities that use chlorofluorocarbons and their labels

There are lots of Three Bond products that use CFCs, some of them are labeled and other are not.

Here is a brief explanation for that.

Generally, aerosol products are often labeled as CFCs.

The aerosol consists of two parts; the "stock solution" which carries out the intended function and the "Propellant" which ejects it. Aerosol products are obligated to specify the elements contained in the propellant as required by the "High Pressure Gas Control Law".

The aerosol products bearing the CFC label that we see on the market, use them as propellants and even if their stock solution contains CFCs, they are not required to be labeled. When a CFC is used in the "stock solution" and carbon dioxide (CO_2) or LPG are used as propellants, this aerosol product does not have to specify the use of CFC.

Next are some examples of Three Bond products in which CFCs are used.

Products that use CFCs as propellants

Tire Pando series, TB1910 and Pando 19C
TB181A, TB181B, and Electron etc.

Products that use CFCs as elements in the stock solution

Brake cleaner (aerosol)
Brake cleaner (liquid)
Freezing checker, Leather wax
Pando 270A

12. Three Bond aerosol product families that use CFCs as propellants

1) Tire Pando series
2) Rust-resistant agents for car body
3) Molybdenum aerosol products
4) Metal mold release agent
5) Personal products

The above aerosol products use either CFC12 or CFC11/12, which can, in most cases, be substituted with either LPG or, LPG/CO_2. In fact development of alternative products using LPG is in progress.

The special features of CFC11 and CFC12 that account for their use in aerosol products are the following.

a) Mutual solubility with the stock solution
b) High specific gravity(liquid specific gravity 1.3-1.5)
c) Nonflammable

When CFC11 and CFC12 are substituted with other elements, it is necessary to resolve these three problems.

《Mutual solubility issue》

The mutual solubility of the stock solution and the propellant greatly influences the properties of the aerosol, such as the spray pattern, stability etc..

In most cases, there is no problem with mutual solubility when substituting CFC11 or CFC 12 with LPG, as a propellant, if the stock solution is a solvent system.

However, there are cases when CO_2 is added to LPG. CO_2 is added when LPG alone does not provide sufficient internal pressure; and when performance in low temperatures is required.

《Specific gravity issue》

The liquid specific gravity of CFC11 and CFC12 is around 1.3 to 1.5. High specific gravity propellants such as CFC11 and CFC12 are advantageous when materials such as molybdenum disulfide, which have a high specific gravity, need to be sprayed and distributed.

If the propellant has a low specific gravity (i.e. a liquid specific gravity of range 0.5 to 0.6) as in the case of LPG, substances with a high specific gravity, such as molybdenum disulfide, tend to precipitate and cake.

Therefore, in some cases, it is necessary to increase the number of steel balls, or modify the stock solution to improve its redispersibility.

《Flammability issue》

As for flammability, the High Pressure Gas Control Law was revised with regard to this matter in August, 1989. As shown in Table 2 and 3, the labeling system was reduced from the five levels (nonflammable, flame retardant, slightly flammable, flammable, very flammable) to 2 levels (i.e. flammable or not).

Moreover, previously, aerosol products used on the human body were required to be nonflammable, a requirement that has been repealed.

However, the flammability issue is not only about the labels, it is also about the practical usage of those products. It is desirable that the release agents of products which will be used near fires or around high temperature objects, such as metal molds, are nonflammable.

The substitution of other aerosol propellants for CFC11 and CFC 12 has been going smoothly overall in spite of the above issues. From now on, it is anticipated that the development and implementation of CFCs alternatives will lead to a complete halt in the use of CFCs, even in indispensable applications.

Three Bond plans to and has taken measures to discontinue the use of CFCs, excluding a small selection of products, by June 1990.

Table 2. Previous levels of flammability according to the High Pressure Gas Control Law

Type of aerosol	Information that should be displayed	
	A	B
1. The explosiveness as determined through testing is 3g or greater per liter, and no flame is emitted during in the flammability test.	Nonflammable	1. Do not store in temperatures of 40°C or greater. 2. Do not discard into the fire after use.
2. The explosiveness as determined through testing is 1g or greater per liter and the length of flame emitted by the flammability test is shorter than 5cm. (Excluding those that meet the conditions of Type 1.)	Flame retardant	1. Do not store in temperatures of 40°C or greater. 2. Do not discard into the fire after use.
3. The explosiveness as determined through testing is 0.25g or greater per liter and the length of flame emitted by the flammability test is shorter than 25cm. (Excluding those that meet the conditions of Type 2.)	Slightly flammable	1. Do not spray in the direction of any flame. 2. Do not use in large quantities in rooms that have an open flame. 3. Do not store in temperatures of 40°C or greater. 4. Do not discard into the fire after use.
4. The explosiveness as determined through testing is 0.13g or greater per liter and the length of flame emitted by the flammability test is shorter than 45cm. (Excluding those that meet the conditions of Type 3.)	Flammable	1. Do not use on the human body. 2. Do not use near the fire. 3. Do not use in large quantities in rooms that have an open flame. 4. Do not store in temperatures of 40℃ or greater. 5. Do not discard into the fire after use.
5. Other aerosol that do not fit in any of the above categories.	Very flammable	1. Do not use on the human body. 2. Do not use it near the fire or in a house where the fire is used. 3. Do not store in the temperatures of 40°C or greater. 4. Do not discard into the fire after use.

Table 3. New flammability display class of High Pressure Gas Control Law revised in August, 1989

Type of aerosol	Information that should be displayed	
	A	B
No flame is admitted in the flame length test, and it does not contain a flammable gas.		This product is dangerous because it uses high-pressure gas. Please use the following precautions. 1. Do not store in temperatures of 40°C or greater. 2. Do not put into the fire. 3. Use completely and discard.
Other aerosols that do not fit in the above category.	Flammable, Watch out for fire	This is a flammable product that contains a high-pressure gas. Please use the following precautions. 1. Do not spray in the direction of any flame. 2. Do not use around any open flames, stoves or heaters. 3. Do not use it in large quantities indoors by the use of the fire. 4. Do not store in temperatures of 40°C or greater. 5. Do not put into the fire. 6. Use completely and discard.

13. Alternative CFCs (propellant, refrigerant, blowing agents)

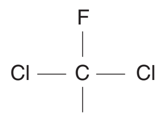
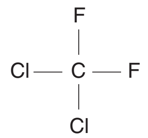
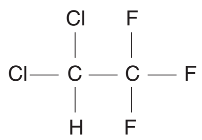
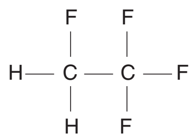
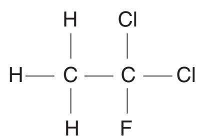
We talked about CFCs that are used as propellants in Chapter 12, and we would like to look at some of the alternatives below.

There are two types of fluorocarbons that are expected to replace CFCs in the future. They are fluorocarbons that do not contain chlorine, the culprit of ozone depletion in the ozone layer and fluorocarbons that contain hydrogen so that they break down in the atmosphere before reaching the stratosphere.

HFC134a, a fluorocarbon that does not contain chlorine, is a substitute for CFC12. As for fluorocarbons that contain hydrogen; there are HCFC123 and HCFC141b which will take its place.

These alternative CFCs undergo testing to ensure their safety and it is expected that they will be ready for use in 4 to 5 years.

Table 4. Currently used CFCs and their substitute

	Properties		Structural formula	Remarks
CFC11	Boiling point Liquid specific gravity (25°C) Flammability ODP[*1] Toxicity [*2]	23.8°C 1.48 Nonflammable 1.0 5a		Propellant, refrigerant, blowing agent, cleaner
CFC12	Boiling point Liquid specific gravity (25°C) Flammability ODP Toxicity	–29.8°C 1.31 Nonflammable 1.0 6		Propellant, refrigerant, and blowing agent
HCFC 123	Boiling point Liquid specific gravity (25°C) Flammability ODP Toxicity	27.5°C 1.46 Nonflammable (< 0.05)[*3] Under investigation		Promising as a substitute of CFC 11
HFC 134a	Boiling point Liquid specific gravity (25°C) Flammability ODP Toxicity	–26.3°C 1.21 Nonflammable 0 Under investigation		Promising as a substitute of CFC 12.
HCFC141b	Boiling point Liquid specific gravity (10°C) Flammability ODP Toxicity	32°C 1.25 Flammable (< 0.05) Under investigation		Substitute for CFC 11

*1: ODP = Ozone Depletion Potential

*2: Toxicity = Underwriter's Laboratories Group No.
This value shows the toxicity of a gassy compound. There are levels, 1 means extremely poisonous (5 minutes of contact with the gas or steam of 0.5 - 1.0% concentration could result in the death or serious injury.), and 6 means very low toxicity (there is no damage caused after 2 hours contact with the gas or steam of 0.5 - 1.0% concentration.). (Example: SO_2:1, NH_3:2, CH_3Cl:4, CO_2:5)

*3: The numbers in the brackets are estimated values

14. Three Bond product families that uses CFC as a cleaner thinner (stock solution element)

1) Brake cleaners
2) Wax group for leathers and tires etc.
3) Parts cleaners
4) Freezing checker

In the above products CFC113 is used for the following reasons.

(1) Stable in heat (nonflammable)
(2) Little influence on metals and resins
(3) Excellent solvency in oils and fats
(4) Excellent volatility
(5) Low toxicity

Current CFC regulations apply restrictions to only 5 specific CFCs, however, there is a movement to amend the CFC regulations in June 1990, so that CFCs are restricted based on their ozone depletion potential (ODP). If that happens, then CFCs other than the 5 specified CFC and chlorinated solvents (1.1.1 ? trichloroethane) could also be restricted by the CFC regulations depending on their ODP.

Therefore, CFCs which may be restricted in the future and chlorinated solvents (1.1.1-trichloroethane) should be excluded from the candidates for substitution for the CFC113 used in cleaners, etc..

The control matrix of the solvents used for cleaners and thinners is as follows.

Table 5. Solvent control matrix

		CFC regulations	OPOSP *1	Fire Service Law *4	Other regulations	Remarks
Fluorocarbon system solvent		×	○	○		CFC113 etc
Chlorinated solvent		△ *2	×	○	*3	Trichloroethane and 1.1.1-trichloroethylene, etc.
Water system solvent (surfactant)		○	○	○		Rust and dissolution issues
Hydrocarbon system solvent	Aromatic group	○	×	×		Benzene, toluene, and xylene, etc.
	Aliphatic group	○	△	×		
Alcohol system solvent		○	△	×		
Glycol system solvent		○	△	×		
Ketone system solvent		○	△	×		
Ether system solvent		○	△	×		
Ester solvent		○	△	×		

○ : Not applicable
△ : Some are applicable, some are not applicable
× : Applicable

*1: Ordinance on the Prevention of Organic Solvent Poisoning (Noxiousness index)
*2: The same restrictions that apply to CFCs will be applicable to 1.1.1 – trichloroethane after June, 1990.
*3: The Law Concerning the Examination and Regulation of Manufacture, etc., of Chemical Substances will be applied to trichloroethylene.
*4: The Fire Service Law will be applied to inflammable liquids.

As shown in the table above, non-flammable cleaners are limited to halogen solvents such as chlorofluorocarbon system solvents, chlorinated solvents, or water system solvents (surfactant type). The chlorofluorocarbon system solvents are subject to CFC regulations, and the chlorinated solvents are subject to the Ordinance on the Prevention of Organic Solvent Poisoning (noxiousness index). In addition, water system cleaners have problems with rust, solvent power (detergency) and volatility. It is necessary to consider these matters while taking alternative measures.

《Fire Service Law》

When a flammable liquid is used, the restrictions based on the Fire Service Law are applicable. The Fire Service Law is scheduled for revision in May, 1990.

Table 6 and Table 7 contain information, excerpted from Fire Service Law, about the following areas of class 4 (inflammable liquids); flash point, hazardous material classification and specified quantity.

Table 6. Current Fire Service Law

Flash point	Hazardous material classification	Specified quantity
The ignition point is 100°C or lower or the flash point is –20°C or lower and the boiling point is 40°C or lower.	Special inflammable	50ℓ
Lower than 21°C	Petroleum oils group 1	100ℓ
—	Alcohols	200ℓ
21°C or higher and lower than 70°C	Petroleum oils group 2	500ℓ
70°C or higher and lower than 200°C	petroleum oils group 3	2,000ℓ
200°C or higher	petroleum oils group 4	3,000ℓ
Extracted oil from animals and plants	Animal and plant oil	3,000ℓ

Table 7. Fire Service Law scheduled to be revised in May, 1990

Flash point	Hazardous material classification		Specified quantity
The ignition point is 100°C or lower or the flash point is –20°C or lower and the boiling point is 40°C or lower.	Special inflammable	—	50ℓ
Lower than 21°C	Petroleum oils group 1	Water-insoluble	200ℓ
		Water soluble	400ℓ
—	Alcohols	—	400ℓ
21°C or higher and lower than 70°C	Petroleum oils group 2	Water-insoluble	1,000ℓ
		Water soluble	2,000ℓ
70°C or higher and lower than 200°C	petroleum oils group 3	Water-insoluble	2,000ℓ
		Water soluble	4,000ℓ
200°C or higher	petroleum oils group 4	—	6,000ℓ
Extracted oil from animals and plants	Animal and plant oil		10,000ℓ

The specified quantities according to the new Fire Service Law have increased significantly compared to the current law, therefore, flammable liquid, especially water soluble flammables will be easy to use.

The Ministry of International Trade contracted the development of a substitute for CFC113 and compatible equipment to the Japan Alcohol Association.

From the description of substitutes for CFC113, it is apparent that CFC113 has many beneficial properties and CFC113 is used in a variety of products with a wide range of applications.

Three Bond is developing alternatives to match the required performance criteria (volatility, inflammation point, solubility, and corrosivity, etc.) for each product. In the cleaner field, we are developing CFC113 substitutes that are strong cleaners, that are flammable liquids, but are not subject to the Ordinance on the Prevention of Organic Solvent Poisoning.

≪ Reference ≫

"CFC control engineering" (1988)

Supervision: CFC control engineering symposium organizing committee

"TRIGGER" ('89-6): Shiro Uchida

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