HCFC-225 as a Drop-in Alternative to CFC-113: Update on its Applications

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1. Introduction

Chlorofluorocarbons (CFCs), 1,1,1-trichloroethane and carbon tetrachloride will be phased out by the end of 1995 based on the Copenhagen amendment to the Montreal Protocol. Therefore, the ozone depleting substance users have selected their alternative technology, and shifted the use to them within one year and a few months.

CFC-113, one of the regulated CFCs, has been widely used as a convenient cleaning agent in various industrial applications such as electronics cleaning, precision cleaning, metal cleaning and dry cleaning, due to its excellent chemical inertness, thermal stability, nonflammability, low toxicity and so on. Various types of alternatives to CFC-113 such as hydrocarbons, alcohols, aqueous and semi-aqueous cleanings have been commercialized. Those alternatives could easily replace some of the CFC-113 applications. However, their properties are different from those of CFC-113. The superior properties of CFC-113 are still very much in demand.

Asahi Glass has developed and commercialized HCFC-225 (a mixture of two isomers: HCFC-225ca and HCFC-225cb) named Asahiklin AK-225® as a drop-in alternative to CFC-113[1, 2]. AK-225 is very similar to CFC-113 in its physical and chemical properties, and is the sole alternative that can be applied to the whole applications of CFC-113 with few changes in the process or cleaning equipment. Thus, AK-225 has been applied as a replacement of CFC-113 in applications where other alternatives cannot be used. AK-225 is regarded now as one of the essential alternatives to phase out CFC-113 smoothly by 1996.

AK-225 production plant has already been operating. Asahi Glass has developed a series of AK-225 products: AK-225® for degreasing (HCFC-225), AK-225AES® for defluxing (an azeotrope of HCFC-225 with ethanol) and AK-225DW® for dewatering (HCFC-225 and surfactant blend).

2. Fundamental Properties

The physical properties of AK-225, AK-225AES and AK-225DW are summarized in Table 1. The boiling point, surface tension and Kauri-Butanol value (KB value) are specifically characterized as the key properties of a cleaning agent. Suitable boiling point in the range from

40 to 60 °C is important to clean parts without raising their temperature to the point where the temperature sensitive elements or materials are affected. Low surface tension enables a cleaning agent to penetrate even into small gaps, and KB value around 30-35 represents a balanced solvency of a solvent, which permits its use in the removal of oil, grease, and dirt from objects without damage to metal, plastic, or elastomeric parts. Furthermore, latent heat of vaporization is also a key property in vapor cleaning. Smaller latent heat of vaporization results in less energy consumption for vaporization of the solvent and the easier drying. As shown in Table1, the physical properties of AK-225 and its blends are very similar to those of CFC-113. AK-225 and its blends can be used with a few or no change of the existing cleaning equipment and procedure for CFC-113.

Table 2 show the effect of AK-225 on 18 kinds of plastics. The compatibilities of AK-225 observed are quite similar to those of CFC-113 except that with PMMA (polymethyl methacrylate). Concerning polycarbonate, there are some cases where AK-225 gives some crack in the parts caused by the residual stress from the injection molding. The effects of AK-225AES on plastics are almost the same as those of CFC-113/ethanol azeotrope.

The effect of AK-225 on various elastomers are shown in Table 3. In general, CFC-113 is rather compatible with elastomers, and AK-225 has similar to slightly less compatibility in comparison to CFC-113.

The compatibility of AK-225 with various metals are summarized in Table 4. The test results clearly show that AK-225 causes no problem with these metals.

Table 5 shows the effect of AK-225 and AK-225AES on adhesives for electronic devices. No adverse effect on the adhesive strength was observed in cleaning process with either AK-225 or CFC-113.

3. Features and Performances in Cleaning Application

The degreasing performance of AK-225 using Houghton Oil is shown in Figure 1. It is proven that AK-225 is equal to CFC-113 in degreasing.

Cleaning performance of the azeotropic mixture of AK-225AES for ionic contamination removal has been tested using various fluxes. Figure 2 shows that the performance of the azeotrope of AK-225AES is almost the same as that of the CFC-113 azeotrope not depending on the fluxes.

The advantage of AK-225 is that it is very similar to CFC-113 in its physical and chemical properties, material compatibilities, and cleaning performances. AK-225 can be used, therefore, as a CFC-113 replacement with relatively few changes in equipment or process operations. From the view point of global environment, however, it is strongly recommended to use AK-225 with recovery system in order to reduce the solvent emission, because AK-225 is as volatile as CFC-113 and has a little threat to the stratospheric ozone layer. New equipments designed for AK-225 to reduce the solvent emission to a minimum level have already been available from several manufacturers in Japan and actually used by many customers.

AK-225 series have been adopted in manufacturing lines by many customers in the world as the substitute for CFC-113 in various fields. These applications include: defluxing of PCBs for automotive, military, space and medical uses which requires high levels of cleanliness; precision cleaning of electric contacts in relays, microswitches and connectors which requires high reliability; precision cleaning of optical components whose surface cleanliness is critical; precision cleaning of assembled units with complex shapes and very small clearances, and so on. These are applications where other alternatives such as aqueous and semi-aqueous cleaning can hardly be applied.

4. Cleaning Procedures for AK-225 Series

1) AK-225

AK-225 has been used as an effective cleaning agent for removal of oils, greases dusts and so on. Especially, it has been applied for degreasing and dust removing of precision components such as coils, relays, connectors and bearings. These components usually have to avoid contact with water, or they can hardly be dried with alternatives other than AK-225 because of their minute and complicated shape.

Cleaning procedures of AK-225 are quite similar to those of CFC-113 as shown in Figure 3. The procedure consists of immersing a work into the boiling solvent, rinsing or spraying with cool solvent and drying in solvent vapor. An existing cleaning equipment for CFC-113 can be used for AK-225 with few changes due to the similar properties between AK-225 and CFC-113. Agitation or ultrasonic cleaning is often used together in the immersing step. Total cleaning time may vary from less than one minute to thirty minutes depending on a required cleanliness level. Typical cleaning time is a few minutes in total. In a certain case, anti corrosive is added into AK-225, then, parts to be cleaned is immersed into the AK-225 to clean and prevent them from corrosion at the same time.

2) AK-225AES: Azeotrope of AK-225 with Ethanol

AK-225AES is an azeotropic mixture of AK-225 and ethanol and mainly used for defluxing PCBs. The cleaning procedures using AK-225AES are the same as those using AK-225. Its cleaning time is often shorter than that with AK-225 in order to minimize the effect on devices mounted on PCBs. In general, no clean flux process is going to replace the solvent defluxing process in many fields. However, the solvent defluxing is necessary to clean high density assemblies which require high reliability. AK-225AES can be used especially for such assemblies.

Many device manufacturers have evaluated the effect of AK-225AES on their devices. For example, it is reported that AK-225 cleaning has less affection than CFC-113 cleaning in swelling the capping elastomer of electrolysis aluminum capacitors and in increasing the chloride ions in them[3].

Depending on the conditions of soldering and/or cleaning, some fluxes and solder pastes developed for CFC-113 cause white residue on PCBs when PCBs are cleaned with AK-225AES. These phenomena are caused by slight differences of solvencies between AK-225 and CFC-113. New fluxes and solder pastes for AK-225AES have already been developed and on market from several manufacturers.

3) AK-225DW: AK-225 and Surfactant Blend

AK-225DW that consists of AK-225, a surfactant and stabilizers can be used for dewatering in the same way as the CFC-113's dewatering grade.

Figure 4 shows a typical dewatering and drying equipment for AK-225DW. AK-225DW is charged in the dewatering sumps and AK-225 is charged in the other sumps. The procedures are as follows. Wetted parts are immersed in the dewartering sumps. Water adhering to the surface of the parts is separated by the surfactant in AK-225DW. The water rises to the surface of AK-225DW due to the density difference between them. It is necessary to rinse the treated parts with AK-225 to remove the surfactant which is adhered on the surface of the parts. The rinsing conditions of this procedure is the same as ones described in AK-225. Many customers manufacturing glass lenses, lead frames, some metal parts and so on have used AK-225DW dewatering and drying system after aqueous cleaning.

5. Environmental Acceptability and Toxicological Studies

ODP values of HCFCs are important to evaluate their environmental acceptability. Their life time in the atmosphere plays a key role in determining their ODP and Halocarbon Global Warming Potential (HGWP) values. The reported data are summarized in Table 6[4~7].

All of the toxicological testings of HCFC-225ca and HCFC-225cb planned under PAFT-IV (Program for Alternative Fluorocarbon Toxicity Testing) were completed by the beginning of 1994. Data from acute toxicity studies including inhalation, oral and dermal routes demonstrate that HCFC-225ca and HCFC-225cb have very low acute toxicity as shown in Table 7. The overall evidence from several genotoxicity studies including Ames assay, *in vitro* cromosomal aberation with CHL and human lymphocyte and *in vivo* unscheduled DNA synthesis assay implies that neither isomer is a genetic hazard. In four-week subacute inhalation toxicity study using rats, both compounds were peroxisome proliferators, and caused an enlargement of the liver: HCFC-225ca appeared to be more potent. In fact, using these endpoints, effects were seen with exposures as low as 50ppm. As for HCFC-225cb, the effect level was 5,000ppm. It was decided, therefore, to conduct a detailed, comparative mechanistic study with both compounds[8]. Concerning a peroxisome proliferation, pronounced species differences have been reported by a number of investigators. Male rats appear to be the species and sex most sensitive to chemically induced peroxisome proliferation. Numerous *in vivo* and *in vitro* studies have demonstrated that compared to rodents, higher mammalian species, including humans, are considerably less sensitive or are insensitive to peroxisome proliferators[9]. 28-day inhalation toxicity studies with marmoset, a kinds of primate proved that both HCFC-225ca and 225cb showed no significant effect.

5. Comparison of Energy Efficiency and Cost

Energy efficiency of AK-225, alkali-based aqueous and semi-aqueous cleaning were compared under the operating assumptions shown in Table 8. The azeotrope of HCFC-225 with ethanol needs only an additional recovery system since the existing facilities for CFC-113 can be used just as they are. On the other hand, alkali-based aqueous or semi-aqueous cleaning require new facilities for cleaning, waste water treatment and water deionization. The estimation shows that AK-225 cleaning requires electric energy of only about half of the latter two cleanings.

Figure 5 shows the comparison of relative cleaning cost for PCBs. It indicates AK-225 is relatively inexpensive in cleaning PCBs among the alternatives such as aqueous and semi-aqueous cleaning.

6. Conclusion

Various alternatives to CFC-113 have been proposed. Among them, aqueous or semi-aqueous cleaning is desired in a view point of the ozone layer protection. Those alternatives require, however, additional investment such as replacement of cleaning equipments and facilities for waste water treatment. AK-225 is a family of HCFCs and considered as a transitional alternative which should be phased out by 2020 as described in the Copenhagen amendment to the Montreal Protocol. The properties and performances of AK-225 described above, however, have proven that it is the sole "drop-in" replacement of CFC-113. It is especially suitable for applications where other alternatives cannot be applied, and it can be used with few changes to existing hardwares for CFC-113. It is another big advantage for customers who cannot afford to invest in new facilities. New equipments designed for AK-225 to reduce the emission at a minimum level have been developed. Thus, AK-225 is regarded now as one of the essential alternatives to phase out CFC-113 smoothly by the end of 1995.

AK-225 series have been applied in manufacturing lines by many customers in the world as a substitute for CFC-113 in various applications. AK-225 production plant has already been operating which has the capacity of a few thousands metric tons per year as a mixture of HCFC-225ca and HCFC-225cb. The capacity of the plant will be increased to meet the expected worldwide requirements.

References

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Table 1 Properties of AK-225 Series

	AK-225	AK-225AES	AK-225DW
Boiling Point (°C)	54	52	54
Freezing Point (°C)	-131	-138	-47 *3
Density (g/cm^3) *1	1.55	1.49	1.54
Viscosity (cps) *1	0.59	0.61	0.63
Surface Tension (dyne/cm) *1	16.2	16.8	16.8
Latent Heat of Vaporization (cal/g) *2	34.6	40.6	36.5
Relative Evaporation Rate (Ether=100)	90	81	90
Specific Heat (cal/g·°C)	0.24	0.27	0.26
Flash Point (°C)	None	None	None
KB Value	31	41	31

*1 at 25°C *2 at b.p. *3 Precipitation Temperature of Surfactant

Table 2 Effect of AK-225 on Plastics

	AK-225	CFC-113
PE(LD)	1	1
PE(HD)	1	1
PP	1	1
PC	1	0
PVC(Plasticized)	2	2
PS	2	2
PPO	2	2
PMMA	3	0

Plastics with NO EFFECT observed
PVC(Rigid), POM, Phenolic, ABS, Nylon 6
Nylon 66, PET(F.R.), PTFE, PCTFE,Epoxy(F.R.)

Effect Key 0 : No Effect
1 : Slightly Affected
2 : Compatibility should be tested
3 : Probably not suitable

Test Condition ; 3 days at boiling point

Table 3 Effect of AK-225 on Elastomers

	AK-225	CFC-113
Polysulfide Rubber	1	1
Chlorosulfonated Polyethylene	1	1
Fluoro Rubber	2	1
Nitrile Rubber	2	1
Natural Rubber	2	3
Butyl Rubber	2	3
Chloroprene Rubber	2	2
EPDM	2	3
Urethane Rubber	3	2
Silicone Rubber	3	3

Effect Key 0 : No Effect
1 : Slightly Affected
2 : Compatibility should be tested
3 : Probably not suitable

Test Condition ; 3 days at boiling point

Table 4 Compatibility of AK-225 with Metals

	AK-225	CFC-113
Aluminum	None	None
Magnesium	None	None
Zinc	None	None
Copper	None	None
Stainless Steel	None	None
Steel	None	None
Tin	None	None

Test Condition: 7 days at boiling point

Table 5 Effect of AK-225 on Adhesive Strength

	Shear Strength (kgf/cm²)				
	Initial	AK-225	AK-225 AES	CFC-113	CFC-113/ EtOH
UV Curing Anaerobic Adhesive					
A	188.6	178.1	193.2	198.6	196.4
B	296.1	281.7	289.1	289.7	288.1
C	267.3	257.0	256.3	258.0	265.9
D	189.7	190.8	192.6	185.6	183.0
Anaerobic Adhesive E	182.2	186.1	182.7	186.7	188.0
Cyanoacrylate Adhesive					
F	173.7	164.6	170.6	174.1	172.1
G	181.5	180.4	177.1	167.9	178.0
H	233.2	243.0	248.4	233.1	230.8

Data from LOCTITE (JAPAN) CORPORATION
Cleaning Condition: Immersion cleaning (40°C) 1 min, rinse 1 min, drying in vapor 1 min

Tble 6 Environmental Acceptability Studies on HCFC-225s

	225ca			225cb		
	Life Time (year)	ODP	HGWP	Life Time (year)	ODP	HGWP
WMO/AFEAS	2.2~2.7	0.025	0.04	6.7~8.1	0.033	0.15
NASA/NIST (Hampson)	1.5~1.7			5.1		
Phy. Chem. Lab. (A. C. Brown et al)	1.5	~0.01				
Asahi Glass	2	~0.01	0.01~0.03	5 ~ 7	~0.04	0.07~0.1

Table 7 Toxicological Studies on HCFC-225s

	225ca	225cb
Acute Oral Toxicity LD 50 orl-rat	>5g/kg	>5g/kg
Acute Inhalation Toxicity LC 50 ihl-rat 4hr	37,300ppm	36,500ppm
Acute Dermal Toxicity LD 50 skn-rbt	>2g/kg	>2g/kg
Subacute Inhalation Toxicity rat 28days Mimimal Effects	50ppm	5,000ppm
Subacute Inhalation Toxicity marmoset 28days Minor Effects	1,000ppm	5,000ppm
Gene Mutation *in-vitro*	Not Active	Not Active
Chromosomal Damage *in-vitro*	Not Active	Not Active

Table 8 Effect of Cleaning Agents on Energy Efficiencies in Defluxing Process

Operating Assumptions: Operating Time 8 hr/day
PCB Size 300 cm²
Quantity 1,000 boards/day
Cleaning Procedure: Wash-Rinse-Drying or Wash-Water Rinse x 3-Drying

	AK-225AES	AK-225AES	Alkali-Based Aqueous	Hydrocarbon Semi-Aqueous
Facilities Newly Required				
Cleaning	(Existing)	X	X	X
Recovery	X			
Waste Water Treatment			X	X
Water Deionization			X	X
Cleaning Time/PCB (min)	4	4	>15	>15
DI Water (l/min)	0	0	20	20
Waste Water (m³/day)	0	0	10	10
Energy Consumption(kWh/h)	27	13.5	49	51

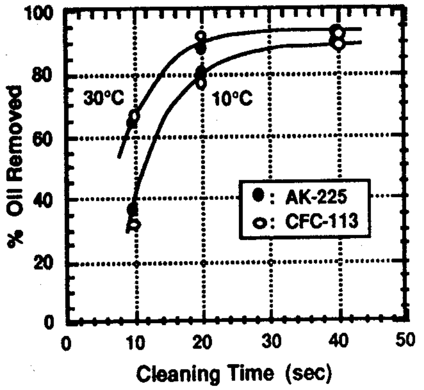

Fig. 1 Degreasing Performance of AK-225

[Drawing Oil (Houghton Oil)]

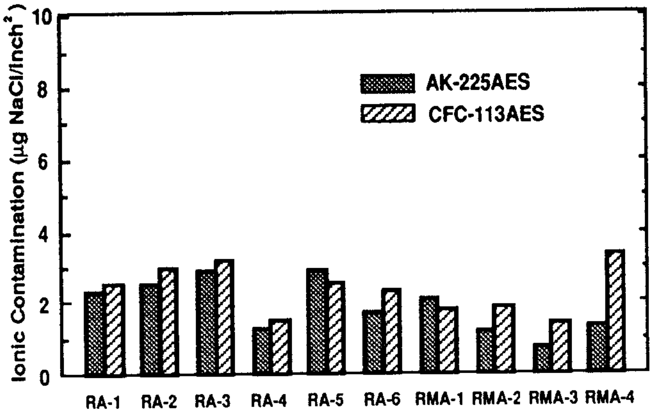

Fig. 2 Defluxing Performance of AK-225AES

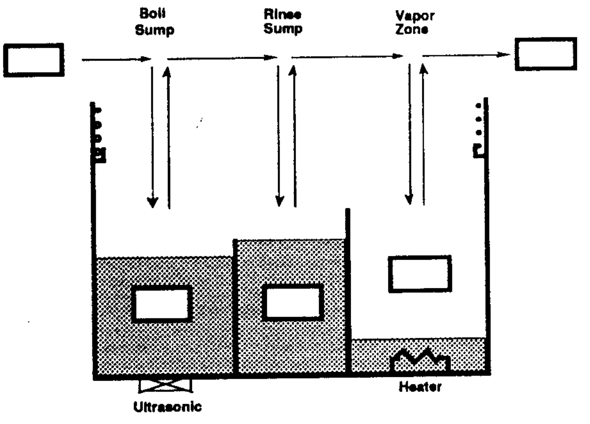

Fig. 3 Typical Open-Top Type Cleaning Equipment for AK-225 and AK-225AES

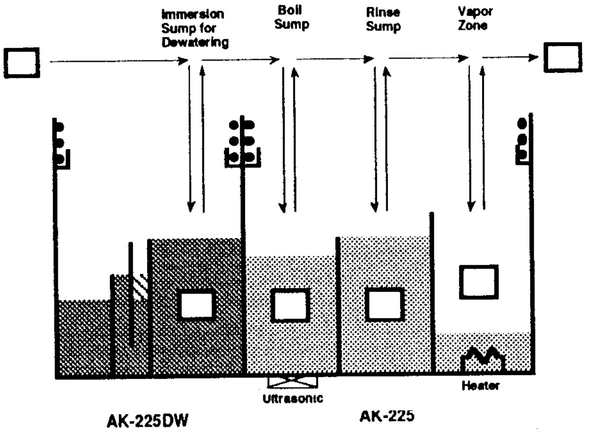

Fig. 4 Dewatering and Drying System for AK-225DW

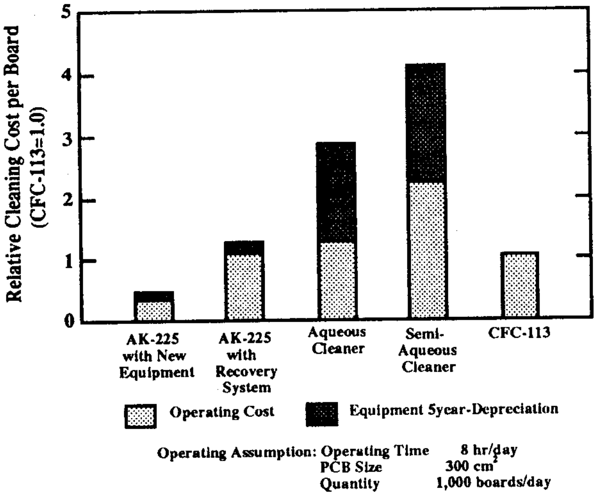

Fig. 5 Comparison of Cleaning Cost for Printed Circuit Boards