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Global Aerosol Events

AEROSOL TODAY®

21-22 SEPTEMBER 2022

FIL - LISBON, PORTUGAL

FEAerosol 2022

WWW.FEAGLOBALEVENTS.ORG

A refill-reuse spray system

A vision for the aerosol industry

AER BEATHA LTD

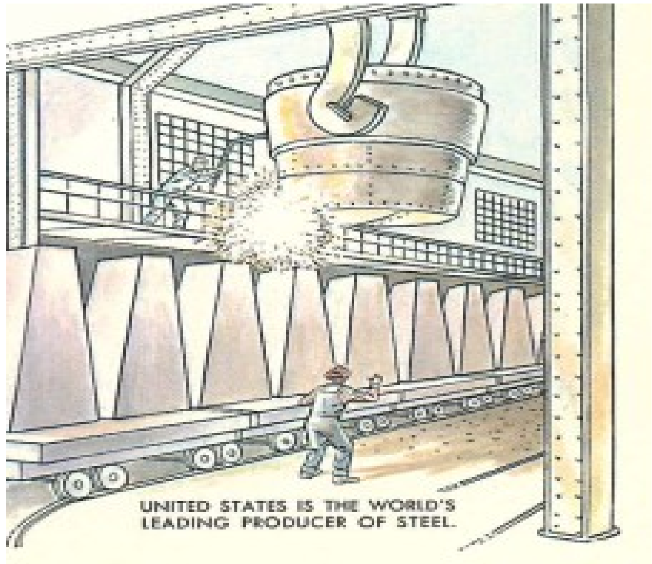
Index

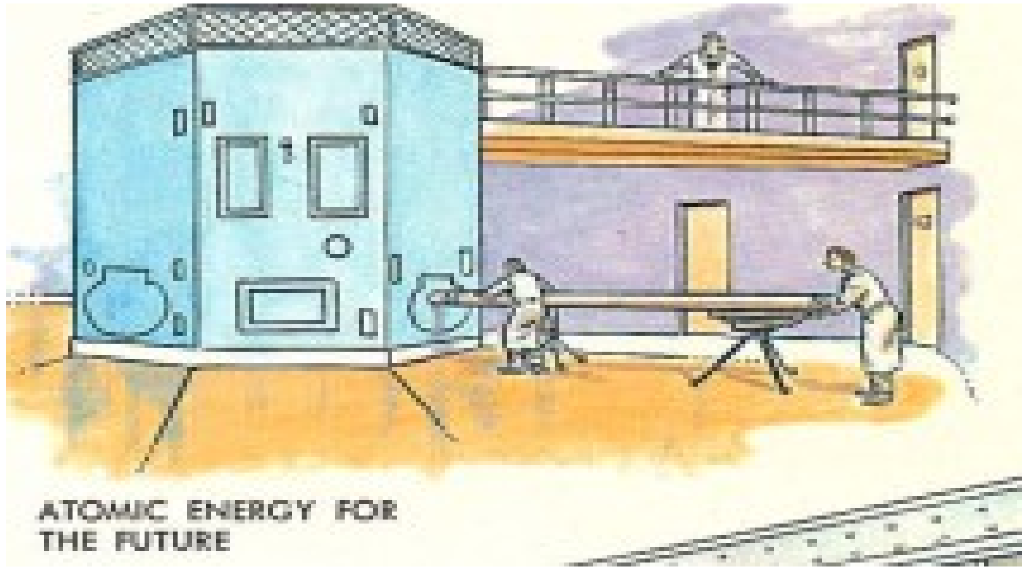
Aerosol Uses & Benefits

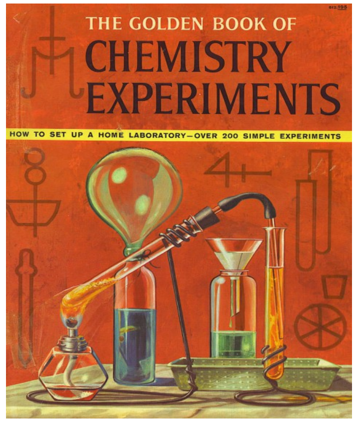
“Aerosols offer a wide range of products from mass-market goods such as cosmetic and household products, to specific aerosol types dedicated for industrial or medical purposes.” FEA

Origin of CFCs & HFCs

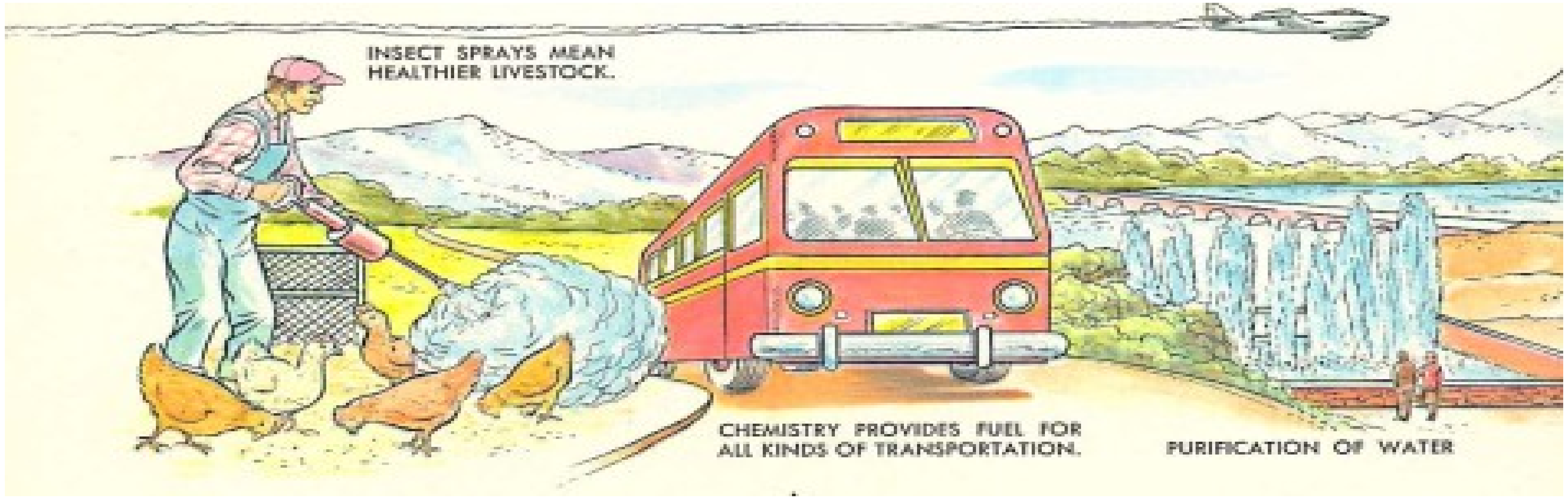

OIL IS THE BASIS FOR COUNTLESS CHEMICAL PRODUCTS.


UNITED STATES IS THE WORLD'S LEADING PRODUCER OF STEEL.


ATOMIC ENERGY FOR THE FUTURE


THE GOLDEN BOOK OF CHEMISTRY EXPERIMENTS

HOW TO SET UP A HOME LABORATORY—OVER 200 SIMPLE EXPERIMENTS


INSECT SPRAYS MEAN HEALTHIER LIVESTOCK.

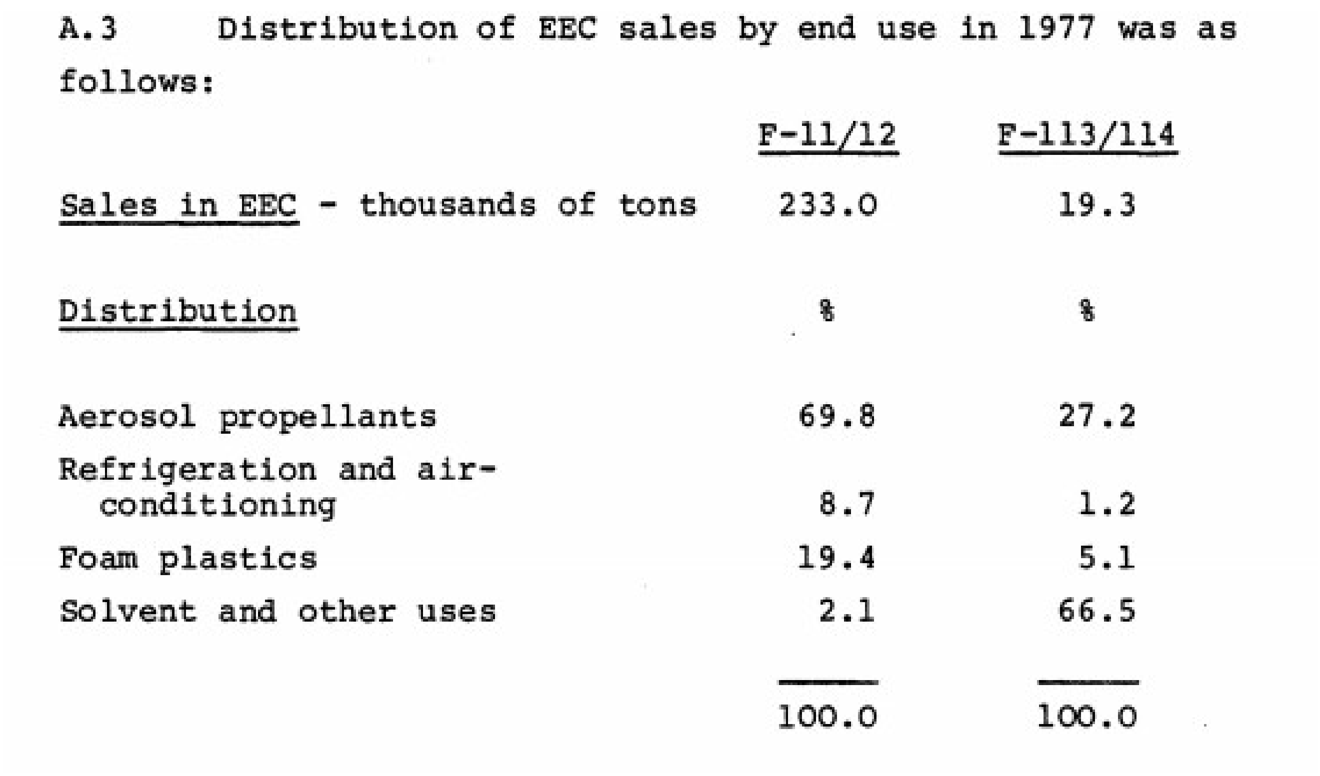
CHEMISTRY PROVIDES FUEL FOR ALL KINDS OF TRANSPORTATION.

PURIFICATION OF WATER

Origin of CFCs & HFCs

In the 1920s, refrigeration and air conditioning systems used compounds such as ammonia, chloromethane, propane and sulphur dioxide as refrigerants. Though effective, the compounds were toxic and flammable, and exposure to them could result in serious injury or death. A team of chemists at Frigidaire led by Thomas Midgely Jr. (1889-1944) worked to develop non toxic, non flammable alternatives to the refrigerants.

CFC Propellant Use 1977



A.3 Distribution of EEC sales by end use in 1977 was as follows:

	F-11/12	F-113/114
Sales in EEC - thousands of tons	233.0	19.3
Distribution	%	%
Aerosol propellants	69.8	27.2
Refrigeration and air-conditioning	8.7	1.2
Foam plastics	19.4	5.1
Solvent and other uses	2.1	66.5
	100.0	100.0

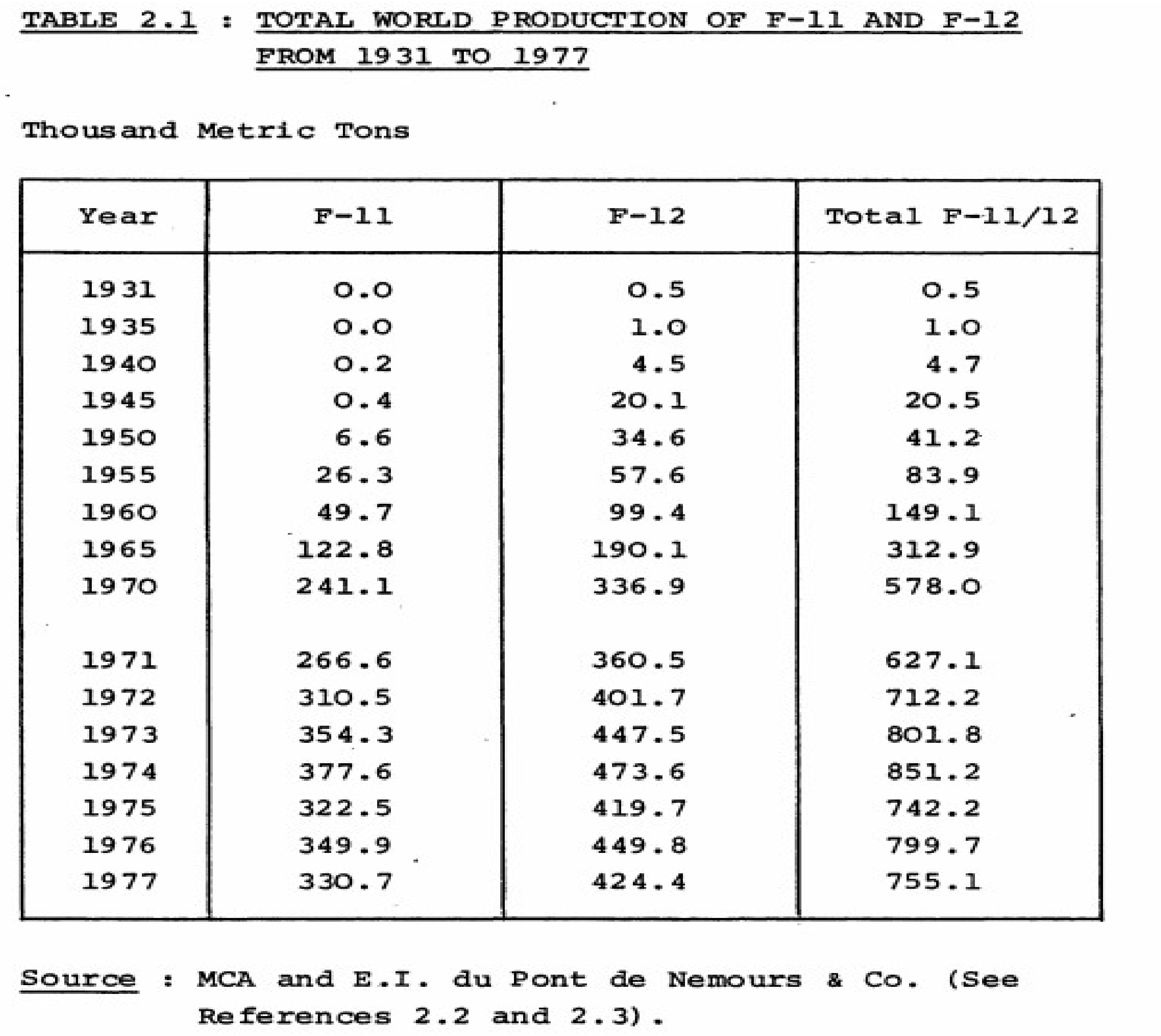


TABLE 2.1 : TOTAL WORLD PRODUCTION OF F-11 AND F-12 FROM 1931 TO 1977

Thousand Metric Tons

Year	F-11	F-12	Total F-11/12
1931	0.0	0.5	0.5
1935	0.0	1.0	1.0
1940	0.2	4.5	4.7
1945	0.4	20.1	20.5
1950	6.6	34.6	41.2
1955	26.3	57.6	83.9
1960	49.7	99.4	149.1
1965	122.8	190.1	312.9
1970	241.1	336.9	578.0
1971	266.6	360.5	627.1
1972	310.5	401.7	712.2
1973	354.3	447.5	801.8
1974	377.6	473.6	851.2
1975	322.5	419.7	742.2
1976	349.9	449.8	799.7
1977	330.7	424.4	755.1

Source : MCA and E.I. du Pont de Nemours & Co. (See References 2.2 and 2.3).

European aerosol production 1977 was 1,874,000,000 units

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Key Properties of CFC Propellants

Non-flammable

Low toxicity

Wide range available

Density (high)

Inexpensive

Key Physical Properties of CFC/HFC

Density

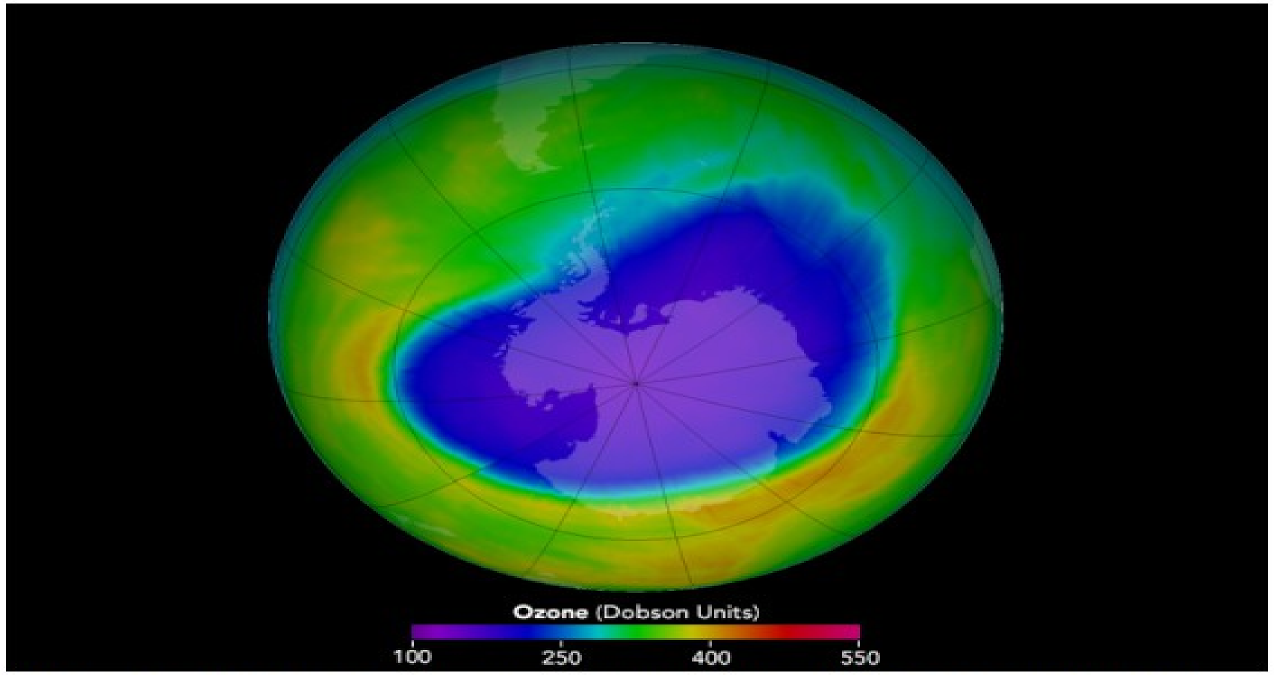
Kauri-Butanol Solvency

P11 co-solvent

Water solubility

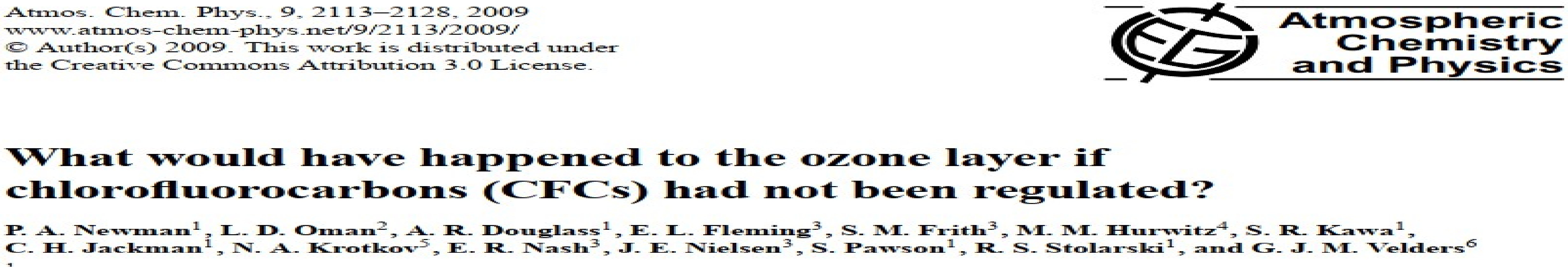
Vapour pressure

Ozone Hole



NASA began measuring Earth's stratospheric ozone layer by satellite in 1979. By the time the Montreal Protocol went into effect in 1989, ozone concentrations (in Dobson units) had declined significantly over the Antarctic, enlarging the ozone hole. Ozone levels have since stabilized, but recovery is still decades away, according to NASA.

Courtesy Jesse Allen (2016), using Suomi NPP OMPS data provided courtesy of Colin Seftor (SSAI) and Aura OMI data provided courtesy of the Aura OMI science team. Suomi NPP is the result of a partnership between NASA, NOAA and the Department of Defense.



Atmos. Chem. Phys., 9, 2113–2128, 2009
www.atmos-chem-phys.net/9/2113/2009/

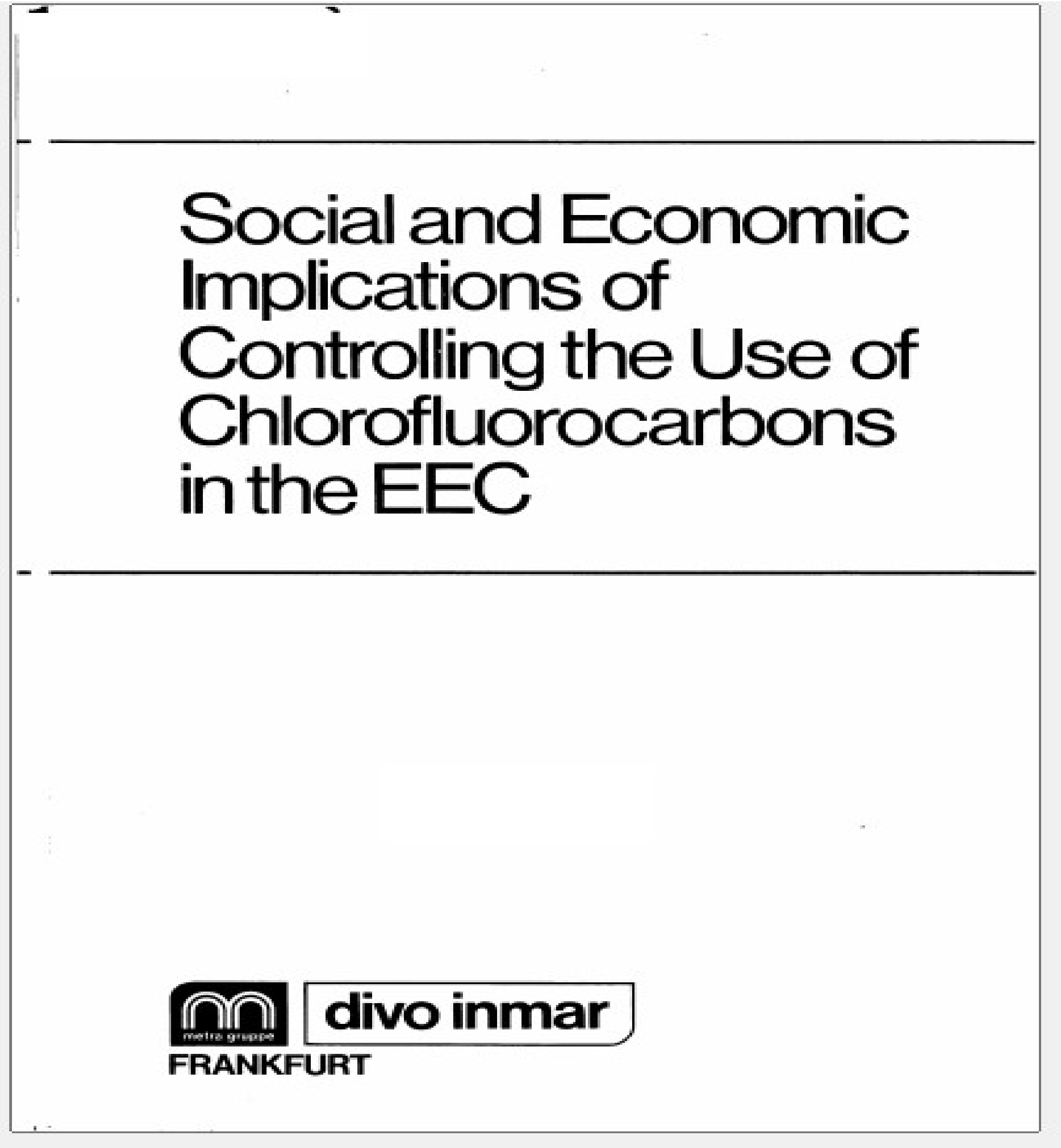
Atmospheric Chemistry and Physics

What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?

P. A. Newman[1], L. D. Oman[2], A. R. Douglass[1], E. L. Fleming[3], S. M. Frith[3], M. M. Hurwitz[4], S. R. Kawa[1],
C. H. Jackman[1], N. A. Krotkov[5], E. R. Nash[3], J. E. Nielsen[3], S. Pawson[1], R. S. Stolarski[1], and G. J. M. Velders[6]

https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/cfcs-ozone.htm

The Implications -1978



Social and Economic Implications of Controlling the Use of Chlorofluorocarbons in the EEC

metra gruppe

divo inmar

FRANKFURT

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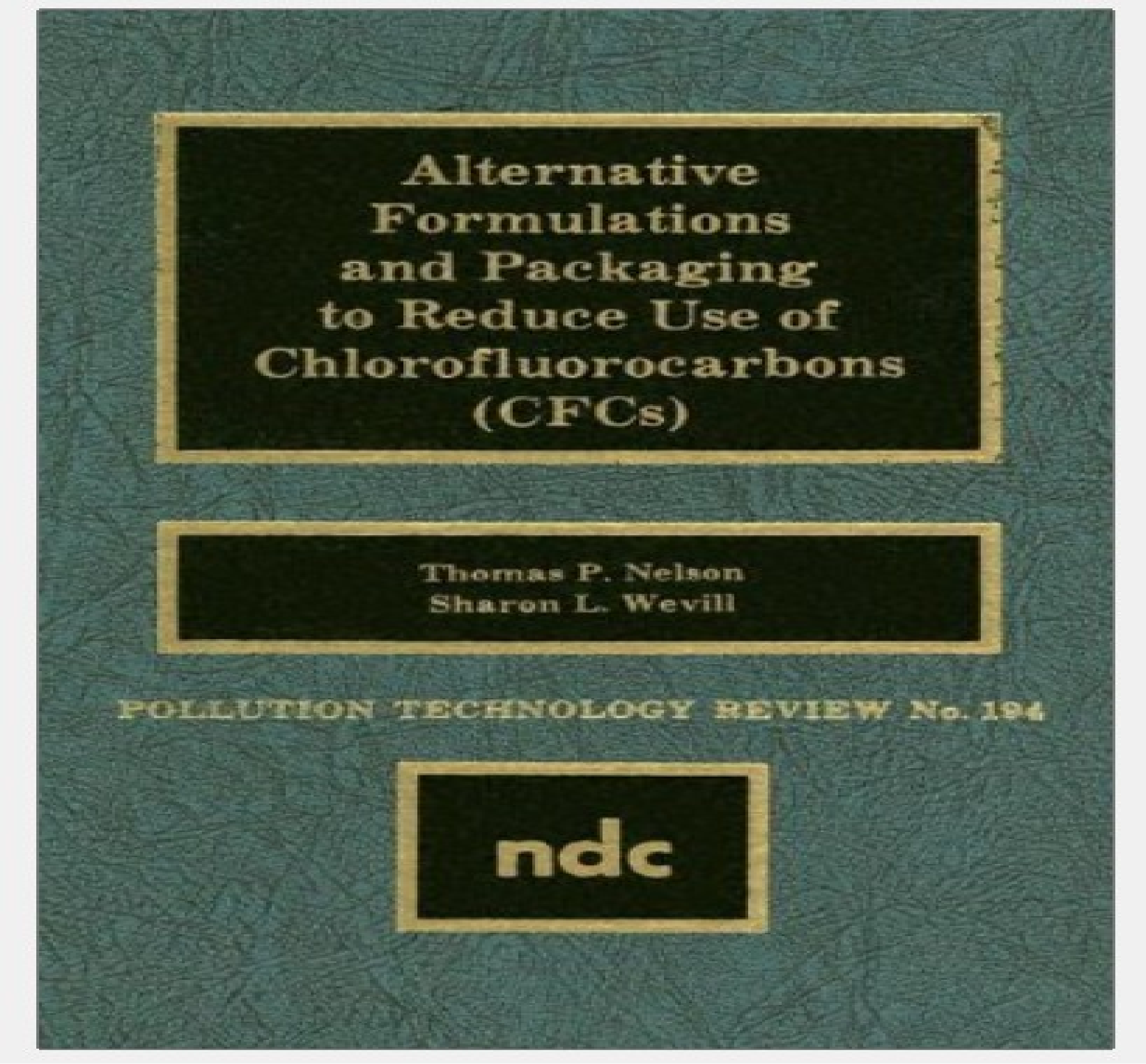
A Formulator's Guide -1990



Alternative
Formulations
and Packaging
to Reduce Use of
Chlorofluorocarbons
(CFCs)

Thomas P. Nelson
Sharon L. Wevill

POLLUTION TECHNOLOGY REVIEW No. 194

ndc

New Propellants

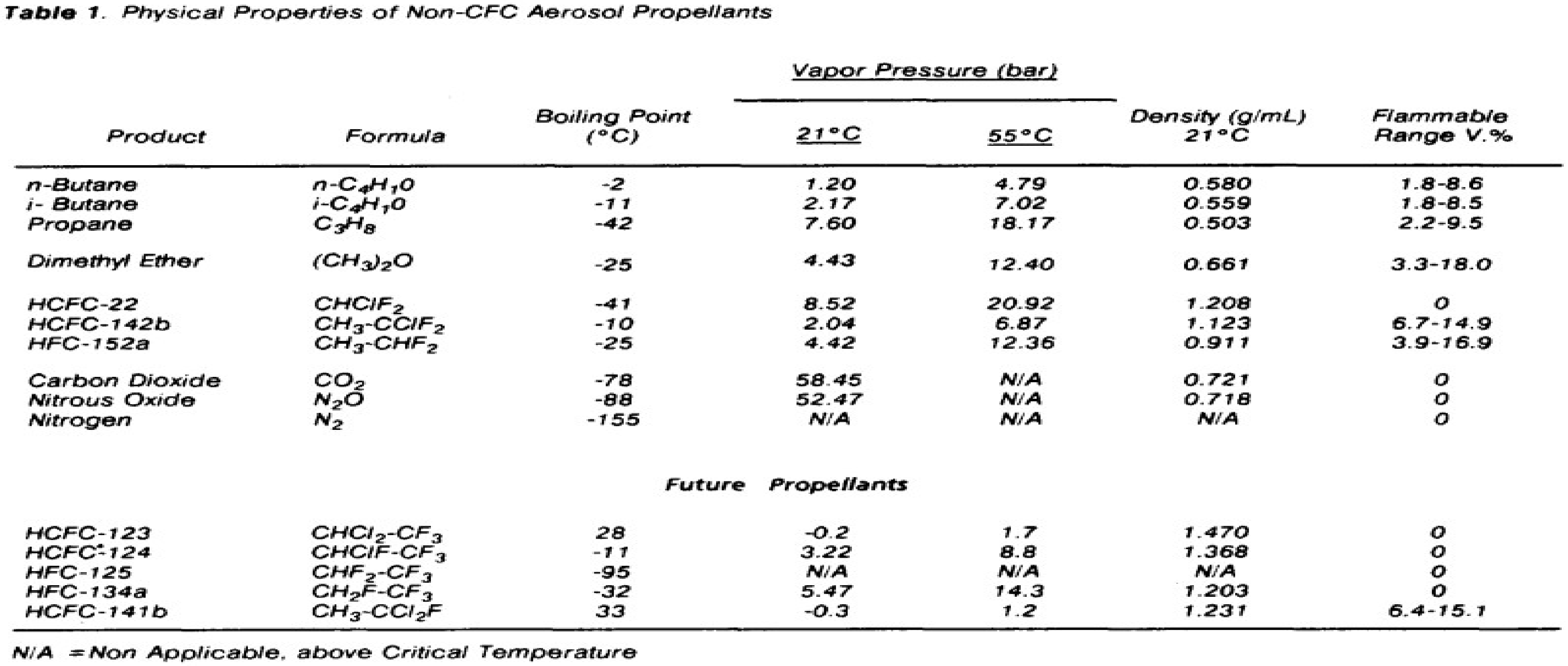


Table 1. Physical Properties of Non-CFC Aerosol Propellants

Product	Formula	Boiling Point (°C)	Vapor Pressure (bar)		Density (g/mL) 21°C	Flammable Range V.%
			21°C	55°C		
n-Butane	n-C_4H_{10}	-2	1.20	4.79	0.580	1.8-8.6
i- Butane	i-C_4H_{10}	-11	2.17	7.02	0.559	1.8-8.5
Propane	C_3H_8	-42	7.60	18.17	0.503	2.2-9.5
Dimethyl Ether	$(CH_3)_2O$	-25	4.43	12.40	0.661	3.3-18.0
HCFC-22	$CHClF_2$	-41	8.52	20.92	1.208	0
HCFC-142b	CH_3-$CClF_2$	-10	2.04	6.87	1.123	6.7-14.9
HFC-152a	CH_3-CHF_2	-25	4.42	12.36	0.911	3.9-16.9
Carbon Dioxide	CO_2	-78	58.45	N/A	0.721	0
Nitrous Oxide	N_2O	-88	52.47	N/A	0.718	0
Nitrogen	N_2	-155	N/A	N/A	N/A	0
		Future	Propellants			
HCFC-123	$CHCl_2$-CF_3	28	-0.2	1.7	1.470	0
HCFC-124	$CHClF$-CF_3	-11	3.22	8.8	1.368	0
HFC-125	CHF_2-CF_3	-95	N/A	N/A	N/A	0
HFC-134a	CH_2F-CF_3	-32	5.47	14.3	1.203	0
HCFC-141b	CH_3-CCl_2F	33	-0.3	1.2	1.231	6.4-15.1

N/A =Non Applicable, above Critical Temperature

EPN600/S2-89/062 Feb.1990

Formulation Challenges

Flammability

Cost

Availability

Toxicology

Solvency

Compatibility - stability

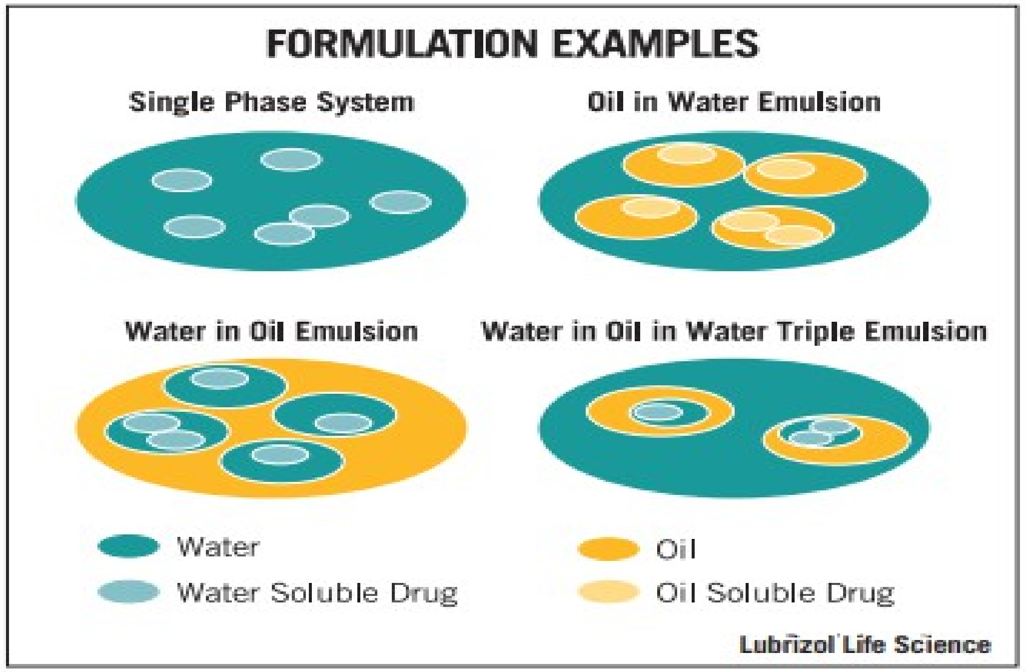
Corrosion

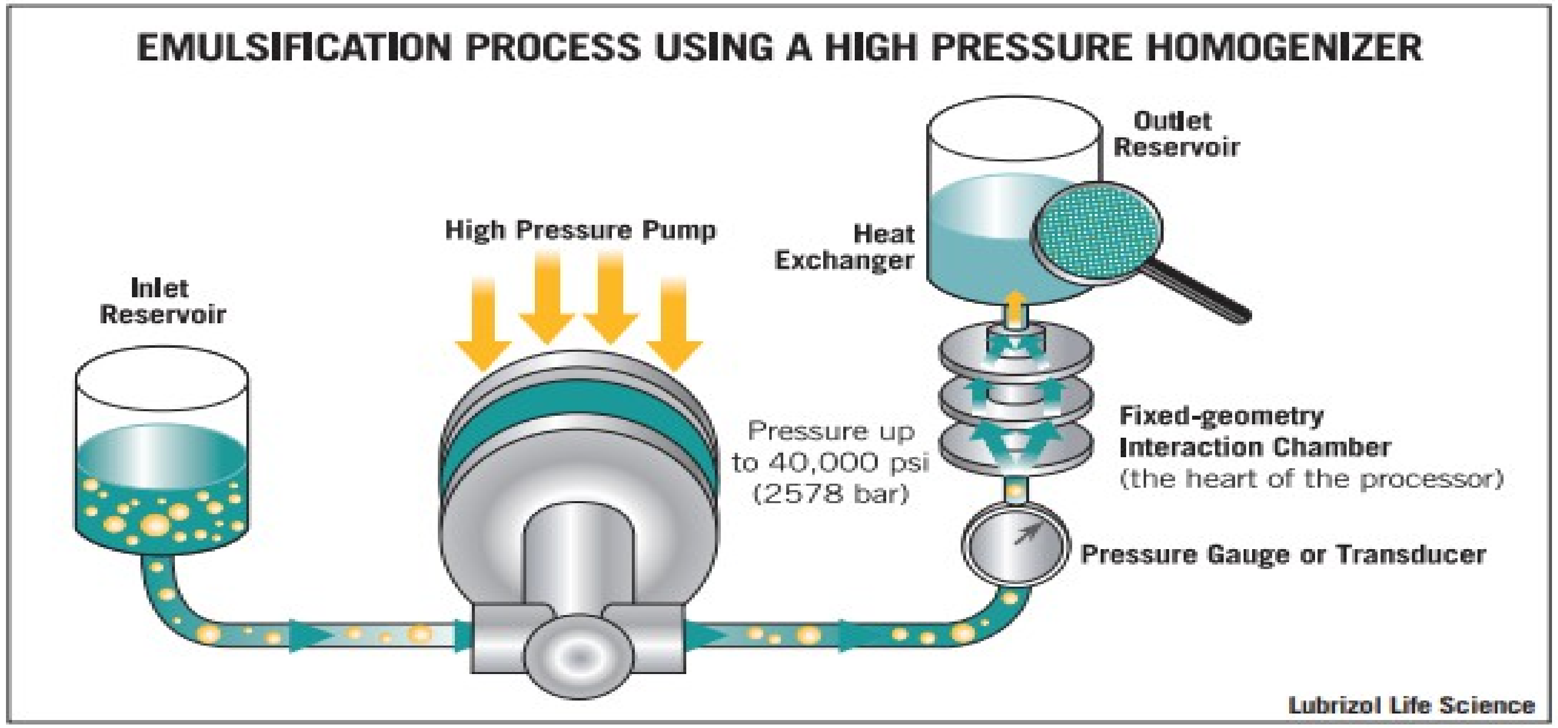
Water-oil emulsions

Performance

Shelf-life

Formulation Challenges





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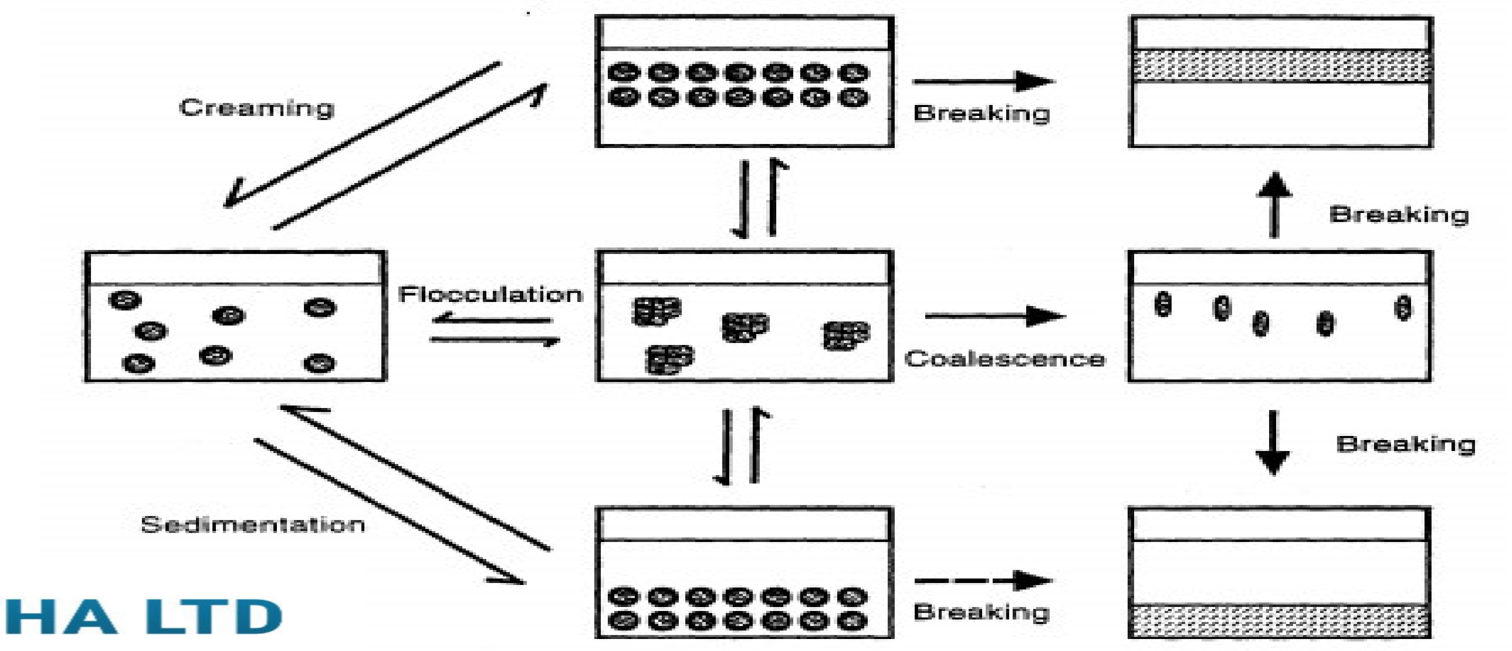
Stokes Law

$$u = 2gr^2(d_1-d_2) / 9\eta$$

Sedimentation rate, u

Viscosity of continuous phase, ŋ
Droplet radius, r
Acceleration of gravity, g
Density of dispersed phase, d1
Density of dispersed phase, d2



Next Challenges

Global Warming Effect – CO2 levels

Volatile Organic Compounds - Ozone

Indoor Environment – health effects

Sustainability

Carbon Dioxide

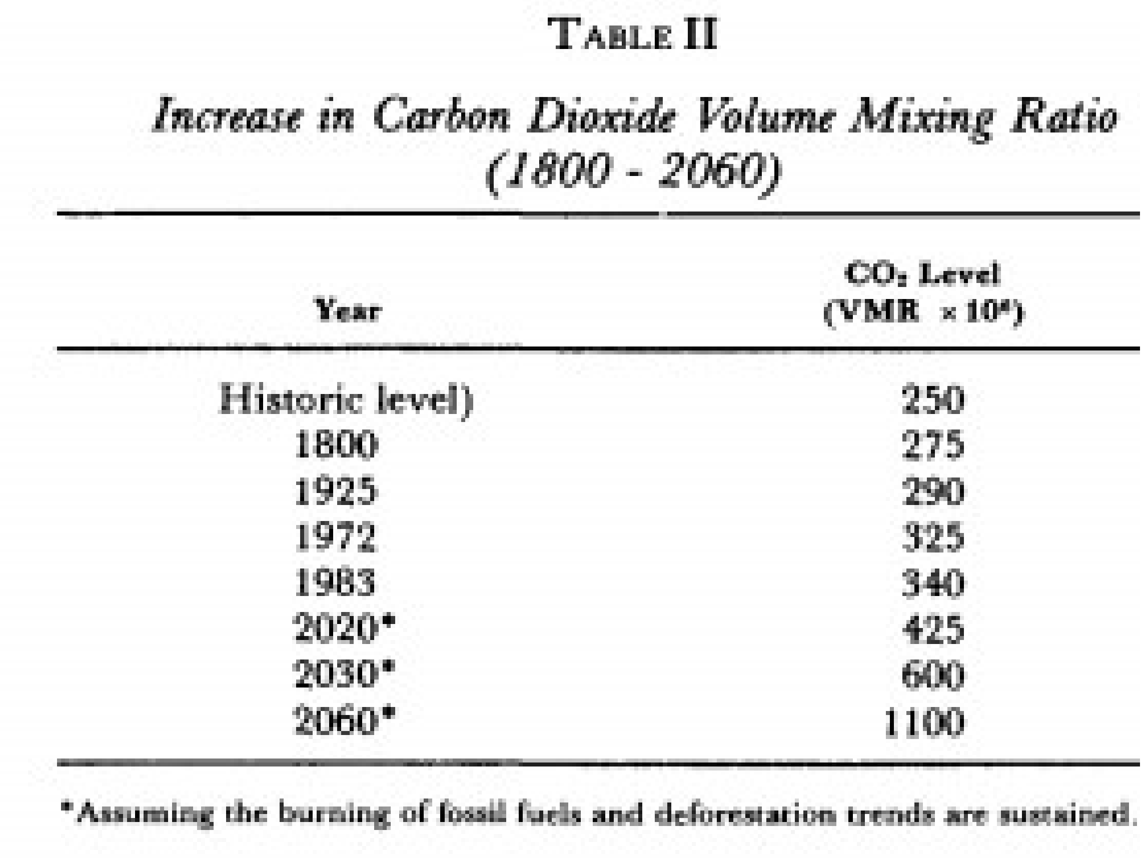
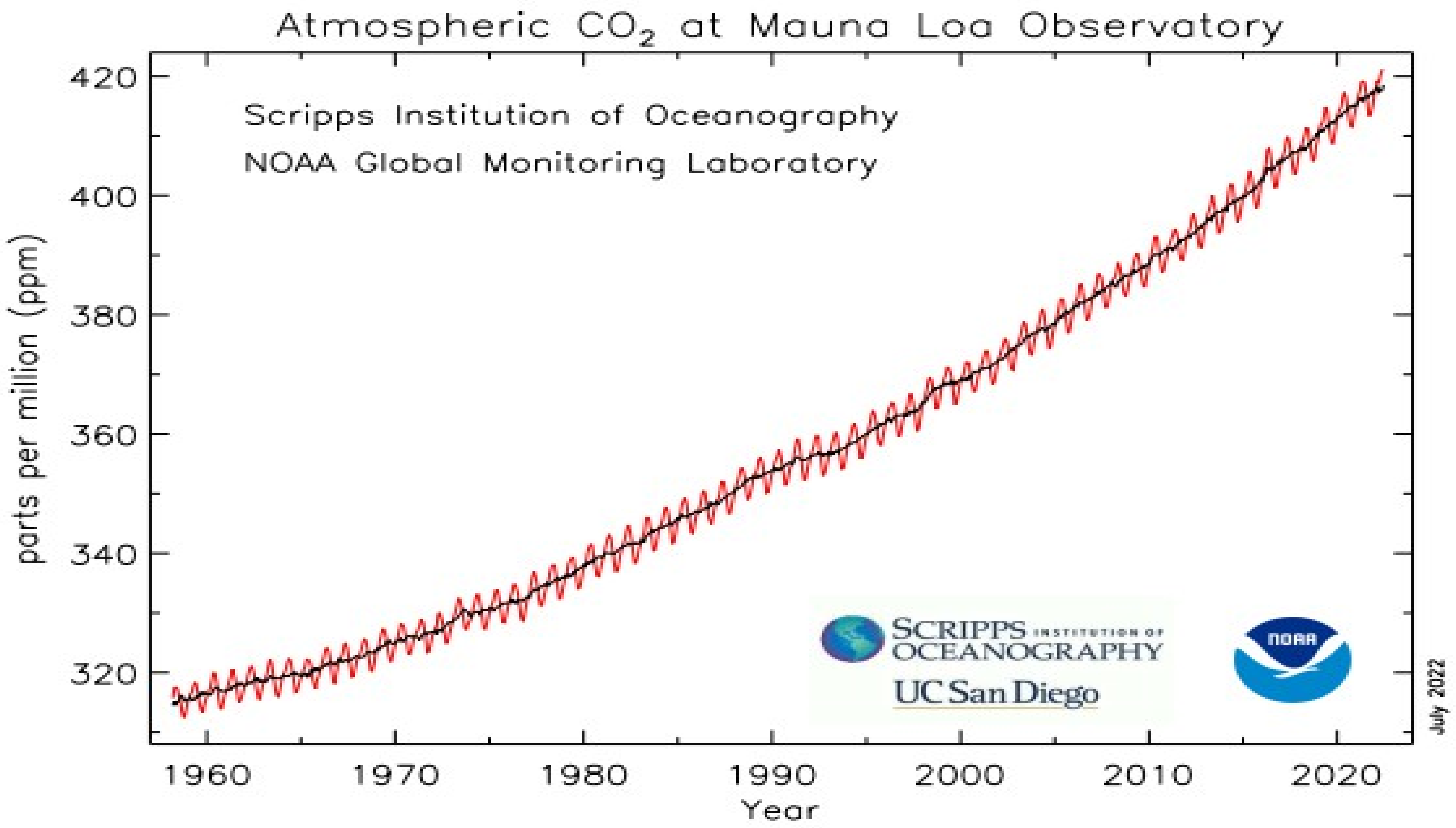


TABLE II

Increase in Carbon Dioxide Volume Mixing Ratio (1800 - 2060)

Year	CO$_2$ Level (VMR × 10^6)
Historic level)	250
1800	275
1925	290
1972	325
1983	340
2020*	425
2030*	600
2060*	1100

*Assuming the burning of fossil fuels and deforestation trends are sustained.



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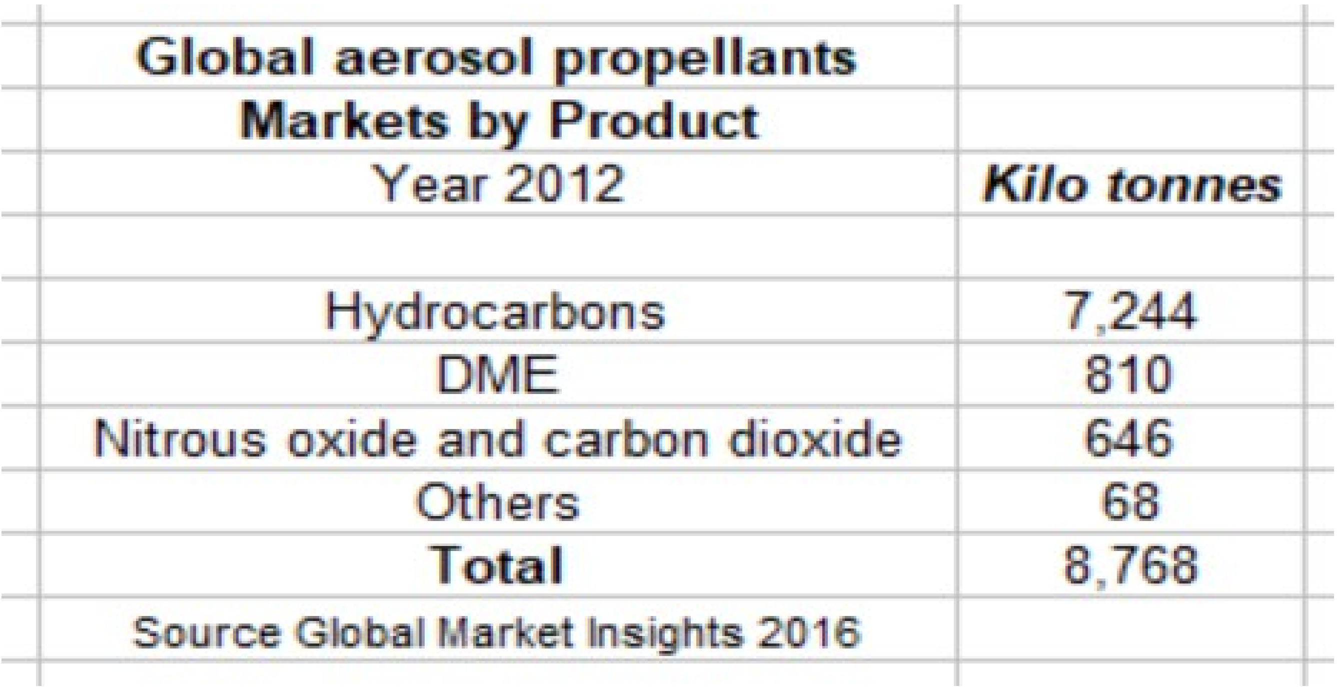
VOCs → Ozone



Global aerosol propellants Markets by Product Year 2012	***Kilo tonnes***
Hydrocarbons	7,244
DME	810
Nitrous oxide and carbon dioxide	646
Others	68
Total	8,768

Source Global Market Insights 2016

Hydrocarbons by Market Year 2012	***Kilo tonnes***
North America	2,142
Latin America	574
Europe	2,697
Asia Pacific	1,679
MEA	152
Total	7,244

Source Global Market Insights 2016

European aerosol production in 2012 was 5.535 billion units, and 5.271 billion units in 2020, According to FEA 2021.

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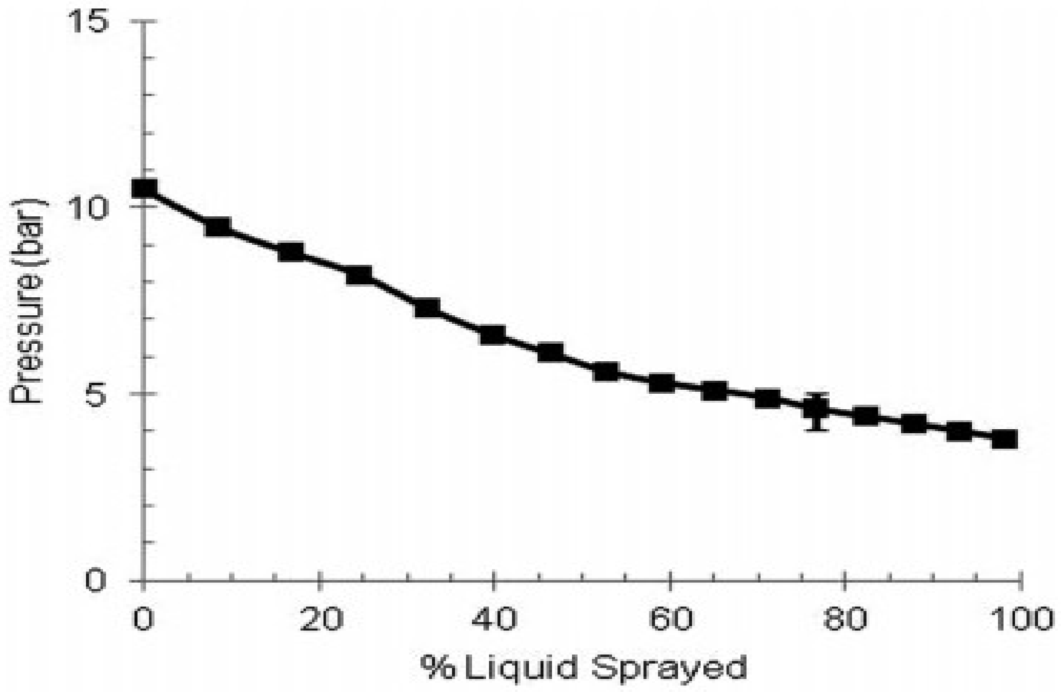
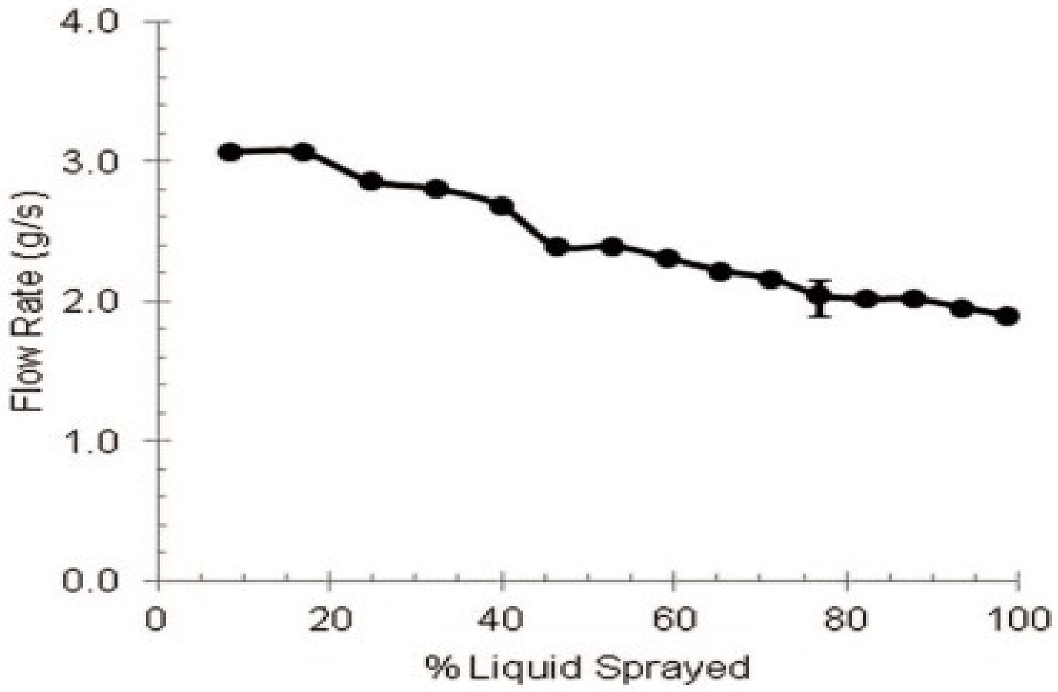
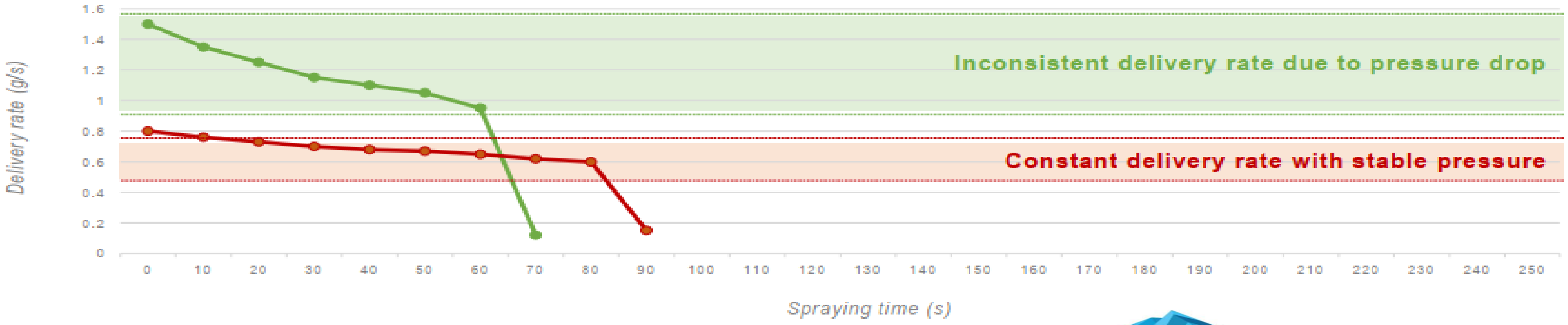
Compressed Gases - Challenge







Source: Coster

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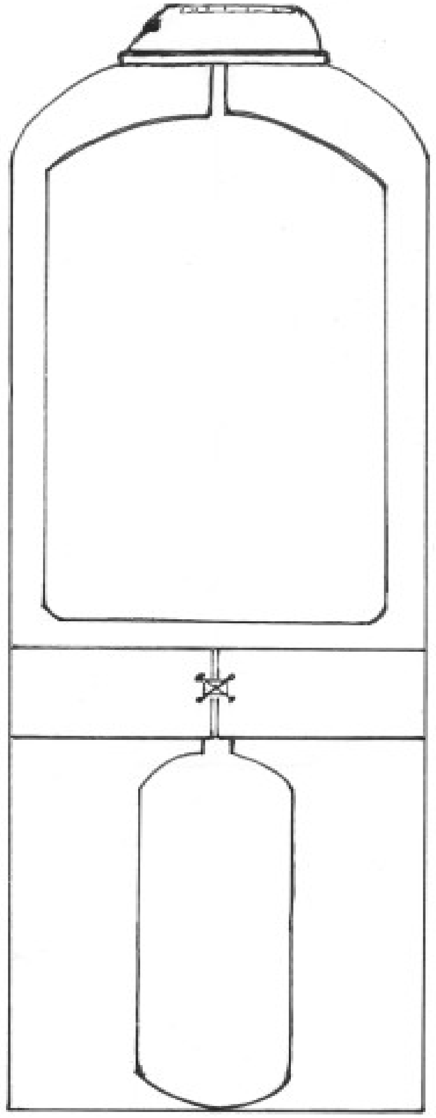
Compressed Gases -> Refill-Reuse



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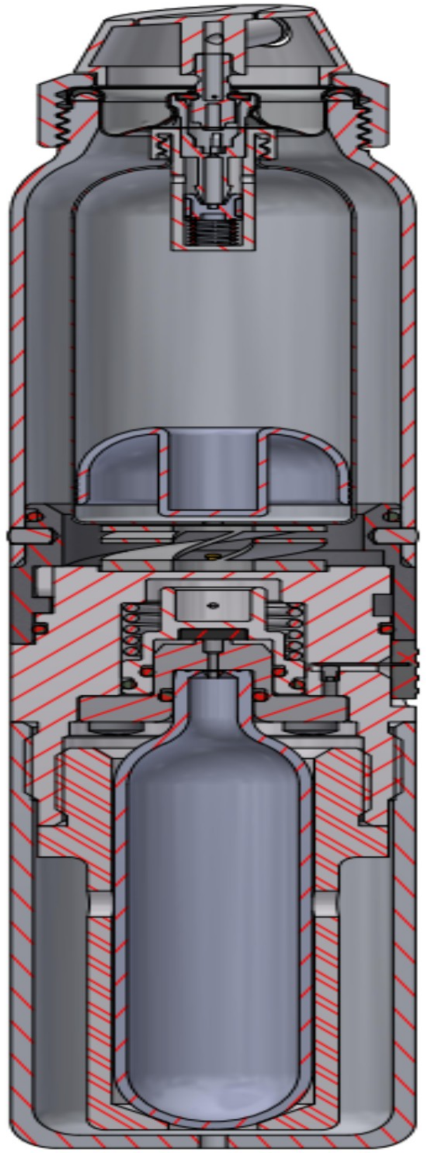
Compressed Gases - Refill-Reuse



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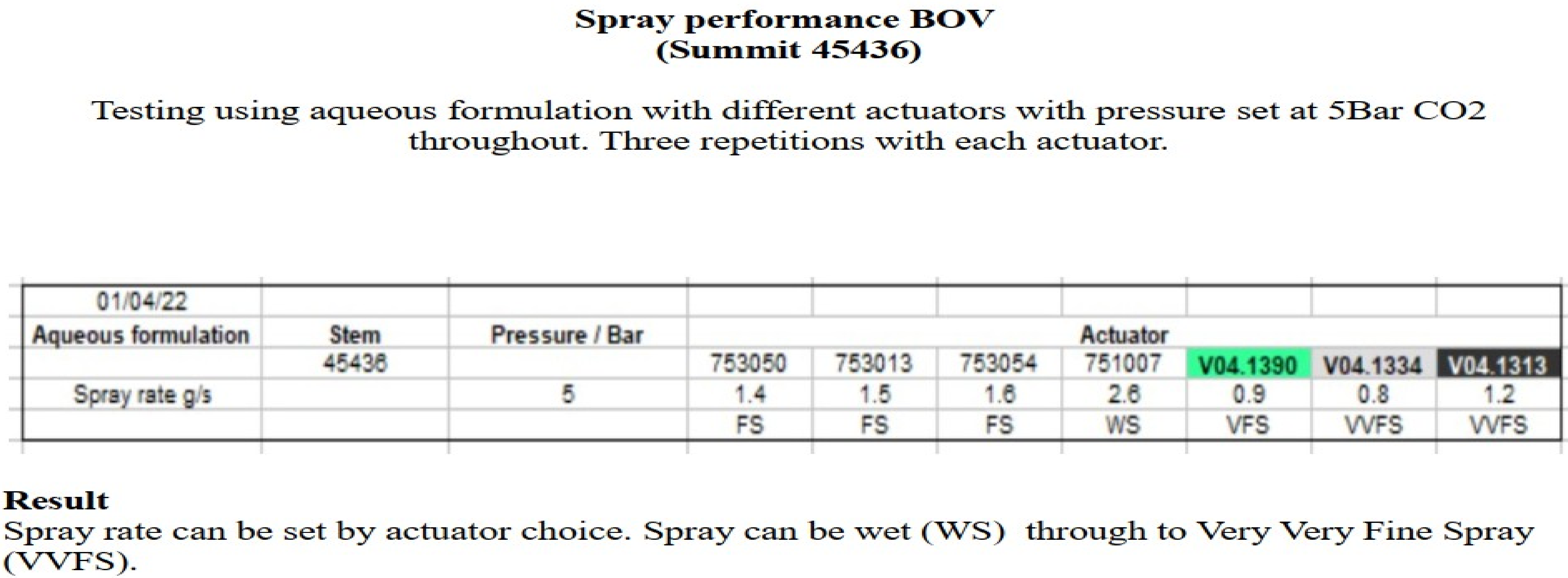
Refill-Reuse Spray Performance



Spray performance BOV
(Summit 45436)

Testing using aqueous formulation with different actuators with pressure set at 5Bar CO2 throughout. Three repetitions with each actuator.

01/04/22									
Aqueous formulation	Stem	Pressure / Bar	Actuator						
	45436		753050	753013	753054	751007	V04.1390	V04.1334	V04.1313
Spray rate g/s		5	1.4	1.5	1.6	2.6	0.9	0.8	1.2
			FS	FS	FS	WS	VFS	VVFS	VVFS

Result
Spray rate can be set by actuator choice. Spray can be wet (WS) through to Very Very Fine Spray (VVFS).

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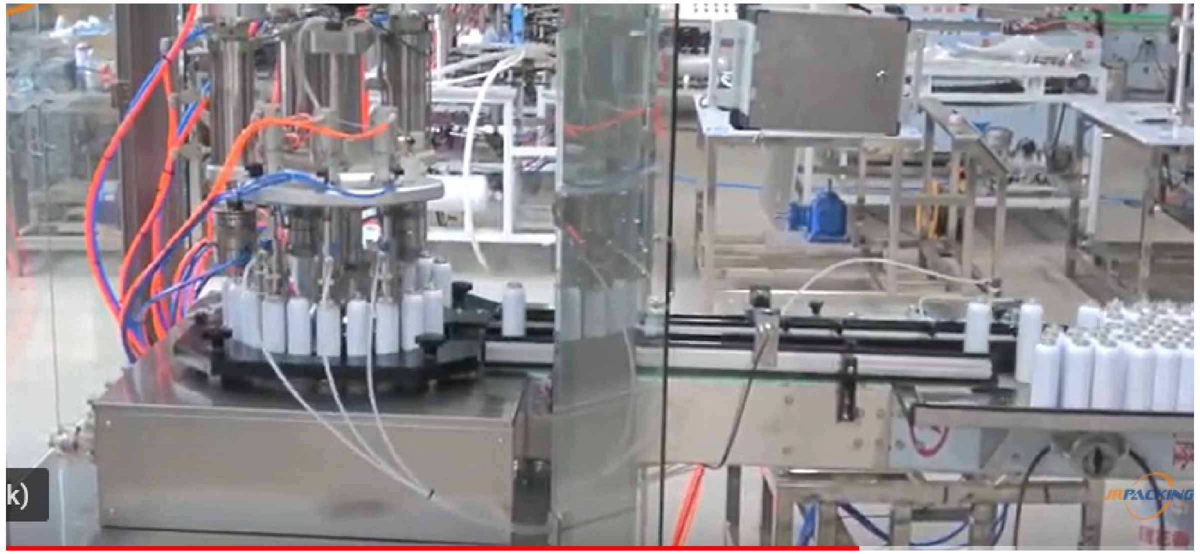
Aerosol Handling and Storage



Aer8® Spray

Refill – Reuse Spray

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Back Up

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Properties of CFC/HFC Propellants

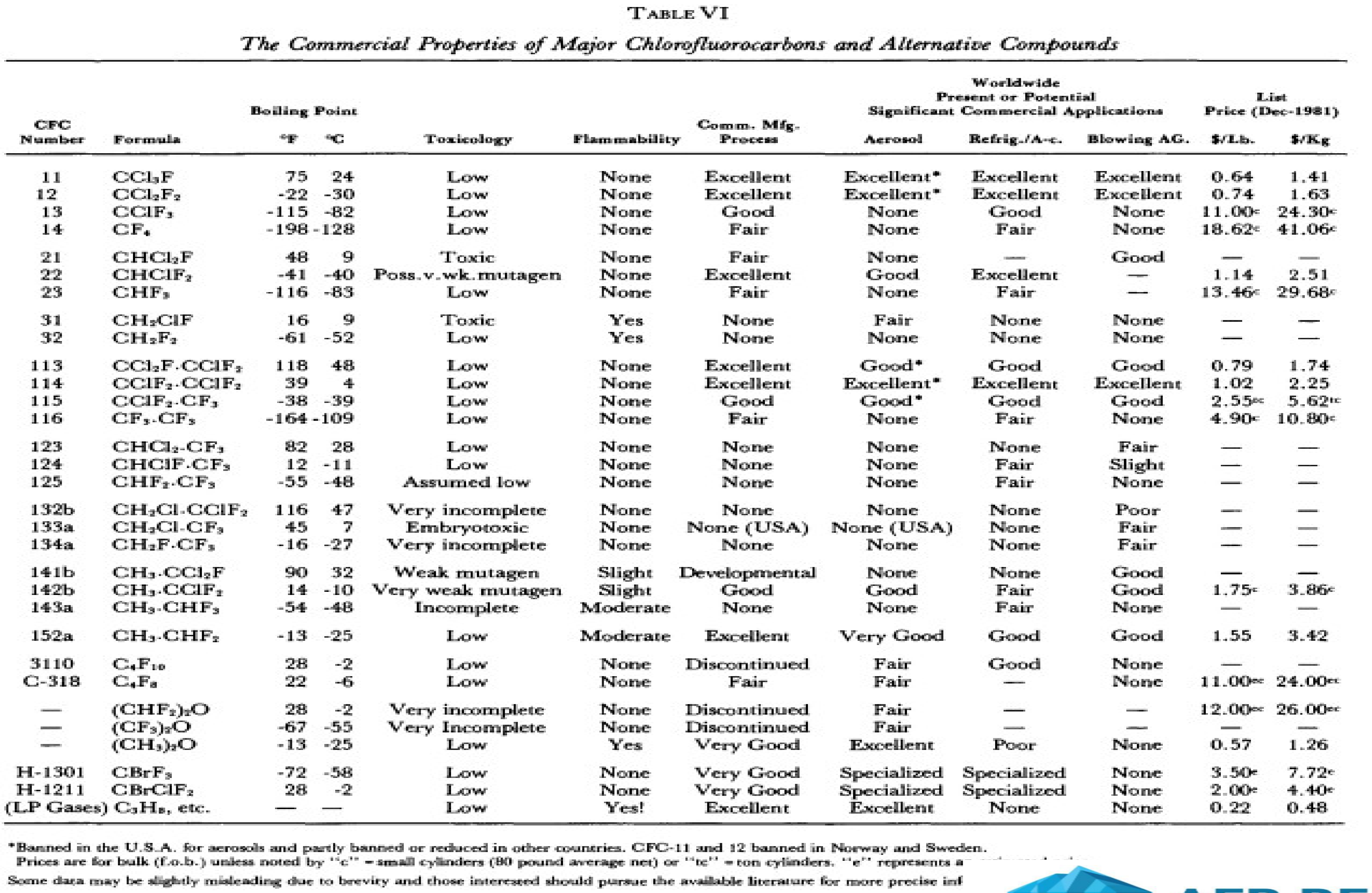

TABLE VI

The Commercial Properties of Major Chlorofluorocarbons and Alternative Compounds

CFC Number	Formula	Boiling Point		Toxicology	Flammability	Comm. Mfg. Process	Worldwide Present or Potential Significant Commercial Applications			List Price (Dec-1981)	
		°F	°C				Aerosol	Refrig./A-c.	Blowing AG.	$/Lb.	$/Kg
11	CCl_3F	75	24	Low	None	Excellent	Excellent*	Excellent	Excellent	0.64	1.41
12	CCl_2F_2	-22	-30	Low	None	Excellent	Excellent*	Excellent	Excellent	0.74	1.63
13	$CClF_3$	-115	-82	Low	None	Good	None	Good	None	11.00^{c}	24.30^{c}
14	CF_4	-198	-128	Low	None	Fair	None	Fair	None	18.62^{c}	41.06^{c}
21	$CHCl_2F$	48	9	Toxic	None	Fair	None	—	Good	—	—
22	$CHClF_2$	-41	-40	Poss.v.wk.mutagen	None	Excellent	Good	Excellent	—	1.14	2.51
23	CHF_3	-116	-83	Low	None	Fair	None	Fair	—	13.46^{c}	29.68^{c}
31	CH_2ClF	16	9	Toxic	Yes	None	Fair	None	None	—	—
32	CH_2F_2	-61	-52	Low	Yes	None	None	None	None	—	—
113	$CCl_2F{\cdot}CClF_2$	118	48	Low	None	Excellent	Good*	Good	Good	0.79	1.74
114	$CClF_2{\cdot}CClF_2$	39	4	Low	None	Excellent	Excellent*	Excellent	Excellent	1.02	2.25
115	$CClF_2{\cdot}CF_3$	-38	-39	Low	None	Good	Good*	Good	Good	2.55^{ec}	5.62^{tc}
116	$CF_3{\cdot}CF_3$	-164	-109	Low	None	Fair	None	Fair	None	4.90^{c}	10.80^{c}
123	$CHCl_2{\cdot}CF_3$	82	28	Low	None	None	None	None	Fair	—	—
124	$CHClF{\cdot}CF_3$	12	-11	Low	None	None	None	Fair	Slight	—	—
125	$CHF_2{\cdot}CF_3$	-55	-48	Assumed low	None	None	None	Fair	None	—	—
132b	$CH_2Cl{\cdot}CClF_2$	116	47	Very incomplete	None	None	None	None	Poor	—	—
133a	$CH_2Cl{\cdot}CF_3$	45	7	Embryotoxic	None	None (USA)	None (USA)	None	Fair	—	—
134a	$CH_2F{\cdot}CF_3$	-16	-27	Very incomplete	None	None	None	None	Fair	—	—
141b	$CH_3{\cdot}CCl_2F$	90	32	Weak mutagen	Slight	Developmental	None	None	Good	—	—
142b	$CH_3{\cdot}CClF_2$	14	-10	Very weak mutagen	Slight	Good	Good	Fair	Good	1.75^{c}	3.86^{c}
143a	$CH_3{\cdot}CHF_3$	-54	-48	Incomplete	Moderate	None	None	Fair	None	—	—
152a	$CH_3{\cdot}CHF_2$	-13	-25	Low	Moderate	Excellent	Very Good	Good	Good	1.55	3.42
3110	C_4F_{10}	28	-2	Low	None	Discontinued	Fair	Good	None	—	—
C-318	C_4F_8	22	-6	Low	None	Fair	Fair	—	None	11.00^{ec}	24.00^{ec}
—	$(CHF_2)_2O$	28	-2	Very incomplete	None	Discontinued	Fair	—	—	12.00^{ec}	26.00^{ec}
—	$(CF_3)_2O$	-67	-55	Very Incomplete	None	Discontinued	Fair	—	—	—	—
—	$(CH_3)_2O$	-13	-25	Low	Yes	Very Good	Excellent	Poor	None	0.57	1.26
H-1301	$CBrF_3$	-72	-58	Low	None	Very Good	Specialized	Specialized	None	3.50^{e}	7.72^{e}
H-1211	$CBrClF_2$	28	-2	Low	None	Very Good	Specialized	Specialized	None	2.00^{e}	4.40^{e}
(LP Gases)	C_3H_8, etc.	—	—	Low	Yes!	Excellent	Excellent	None	None	0.22	0.48

*Banned in the U.S.A. for aerosols and partly banned or reduced in other countries. CFC-11 and 12 banned in Norway and Sweden.
Prices are for bulk (f.o.b.) unless noted by "c" = small cylinders (80 pound average net) or "tc" = ton cylinders. "e" represents a

Some data may be slightly misleading due to brevity and those interested should pursue the available literature for more precise inf

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Physical Properties of CFC/HFC

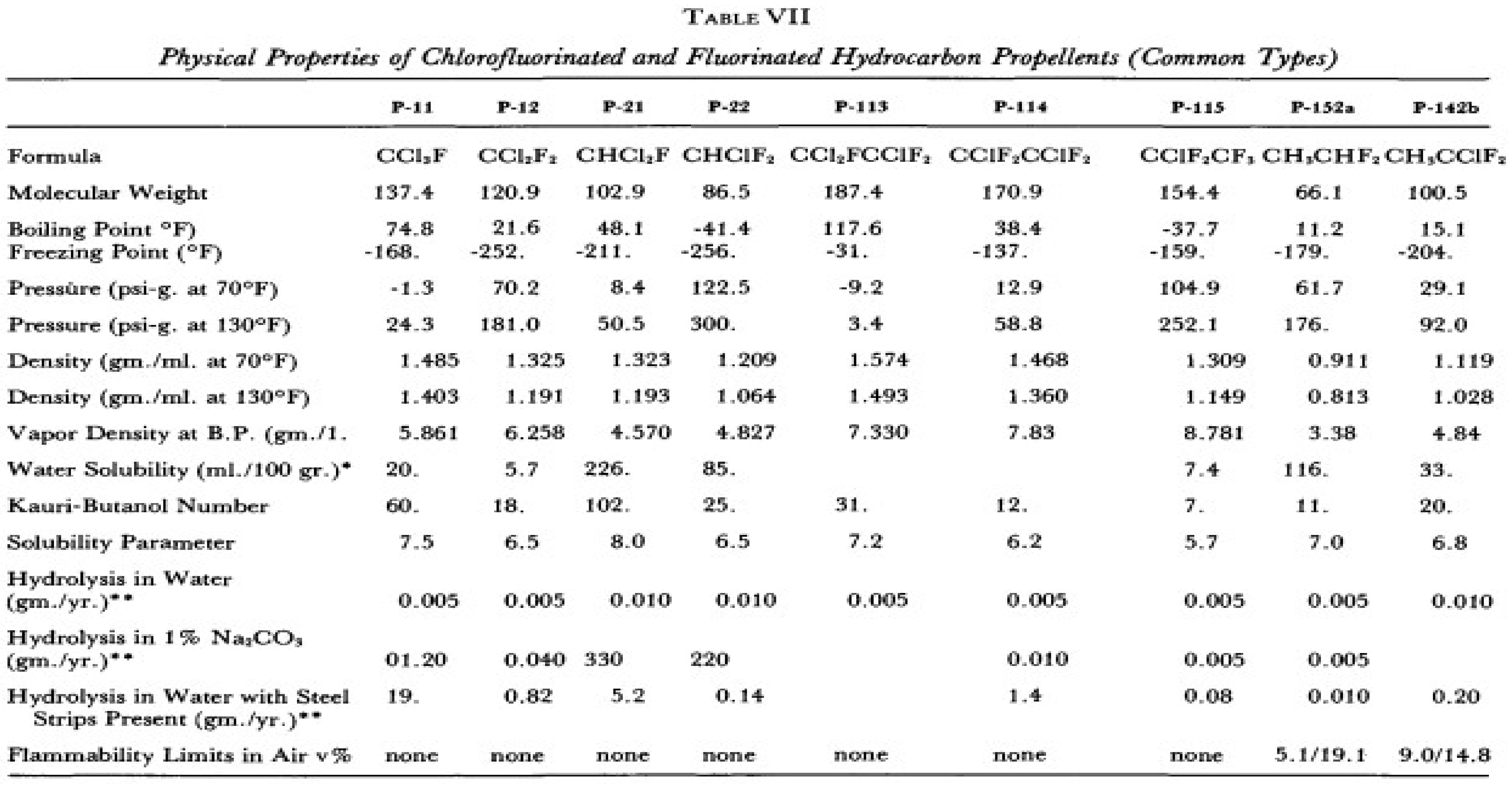

TABLE VII

Physical Properties of Chlorofluorinated and Fluorinated Hydrocarbon Propellents (Common Types)

	P-11	P-12	P-21	P-22	P-113	P-114	P-115	P-152a	P-142b
Formula	CCl_3F	CCl_2F_2	$CHCl_2F$	$CHClF_2$	CCl_2FCClF_2	$CClF_2CClF_2$	$CClF_2CF_3$	CH_3CHF_2	CH_3CClF_2
Molecular Weight	137.4	120.9	102.9	86.5	187.4	170.9	154.4	66.1	100.5
Boiling Point °F)	74.8	21.6	48.1	-41.4	117.6	38.4	-37.7	11.2	15.1
Freezing Point (°F)	-168.	-252.	-211.	-256.	-31.	-137.	-159.	-179.	-204.
Pressûre (psi-g. at 70°F)	-1.3	70.2	8.4	122.5	-9.2	12.9	104.9	61.7	29.1
Pressure (psi-g. at 130°F)	24.3	181.0	50.5	300.	3.4	58.8	252.1	176.	92.0
Density (gm./ml. at 70°F)	1.485	1.325	1.323	1.209	1.574	1.468	1.309	0.911	1.119
Density (gm./ml. at 130°F)	1.403	1.191	1.193	1.064	1.493	1.360	1.149	0.813	1.028
Vapor Density at B.P. (gm./1.	5.861	6.258	4.570	4.827	7.330	7.83	8.781	3.38	4.84
Water Solubility (ml./100 gr.)*	20.	5.7	226.	85.			7.4	116.	33.
Kauri-Butanol Number	60.	18.	102.	25.	31.	12.	7.	11.	20.
Solubility Parameter	7.5	6.5	8.0	6.5	7.2	6.2	5.7	7.0	6.8
Hydrolysis in Water (gm./yr.)**	0.005	0.005	0.010	0.010	0.005	0.005	0.005	0.005	0.010
Hydrolysis in 1% Na_2CO_3 (gm./yr.)**	01.20	0.040	330	220		0.010	0.005	0.005	
Hydrolysis in Water with Steel Strips Present (gm./yr.)**	19.	0.82	5.2	0.14		1.4	0.08	0.010	0.20
Flammability Limits in Air v%	none	none	none	none	none	none	none	5.1/19.1	9.0/14.8

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Key Physical Properties - Density

Density (1.10 to 1.59)

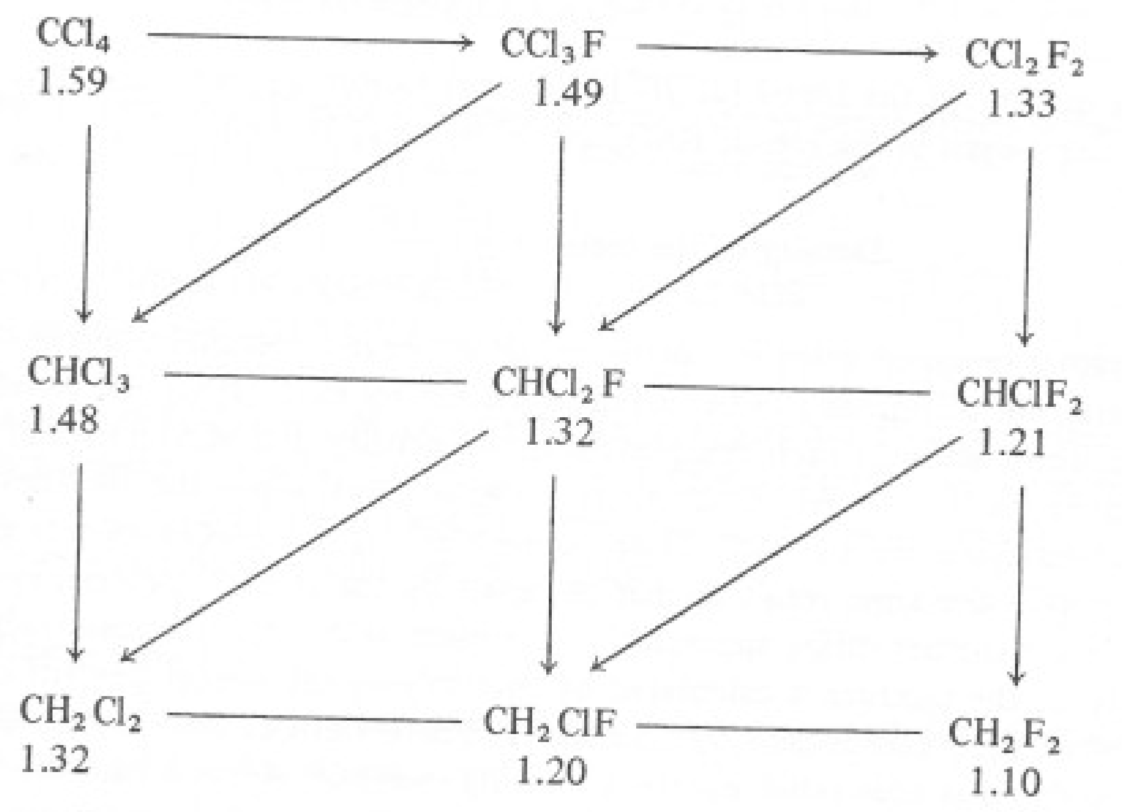

Figure 12-1 Relationship of density to structure.*

*The number under each compound is the density (g/cc) at 70° F.

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Key Physical Properties - Solvency

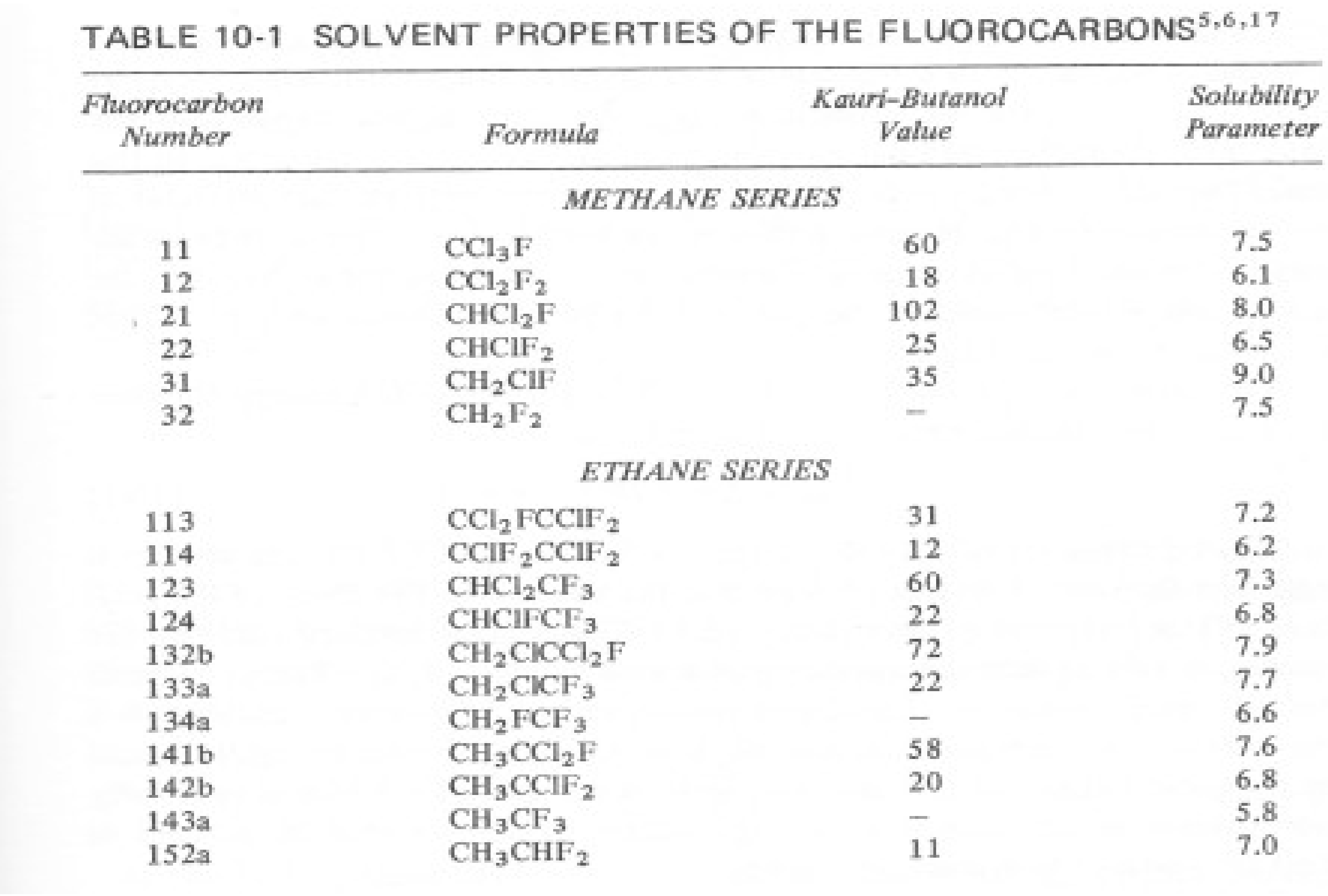

TABLE 10-1 SOLVENT PROPERTIES OF THE FLUOROCARBONS[5,6,17]

Fluorocarbon Number	*Formula*	*Kauri-Butanol Value*	*Solubility Parameter*
	METHANE SERIES		
11	CCl_3F	60	7.5
12	CCl_2F_2	18	6.1
21	$CHCl_2F$	102	8.0
22	$CHClF_2$	25	6.5
31	CH_2ClF	35	9.0
32	CH_2F_2	—	7.5
	ETHANE SERIES		
113	CCl_2FCClF_2	31	7.2
114	$CClF_2CClF_2$	12	6.2
123	$CHCl_2CF_3$	60	7.3
124	$CHClFCF_3$	22	6.8
132b	CH_2ClCCl_2F	72	7.9
133a	CH_2ClCF_3	22	7.7
134a	CH_2FCF_3	—	6.6
141b	CH_3CCl_2F	58	7.6
142b	CH_3CClF_2	20	6.8
143a	CH_3CF_3	—	5.8
152a	CH_3CHF_2	11	7.0

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Solvency - (Kauri-Butanol)

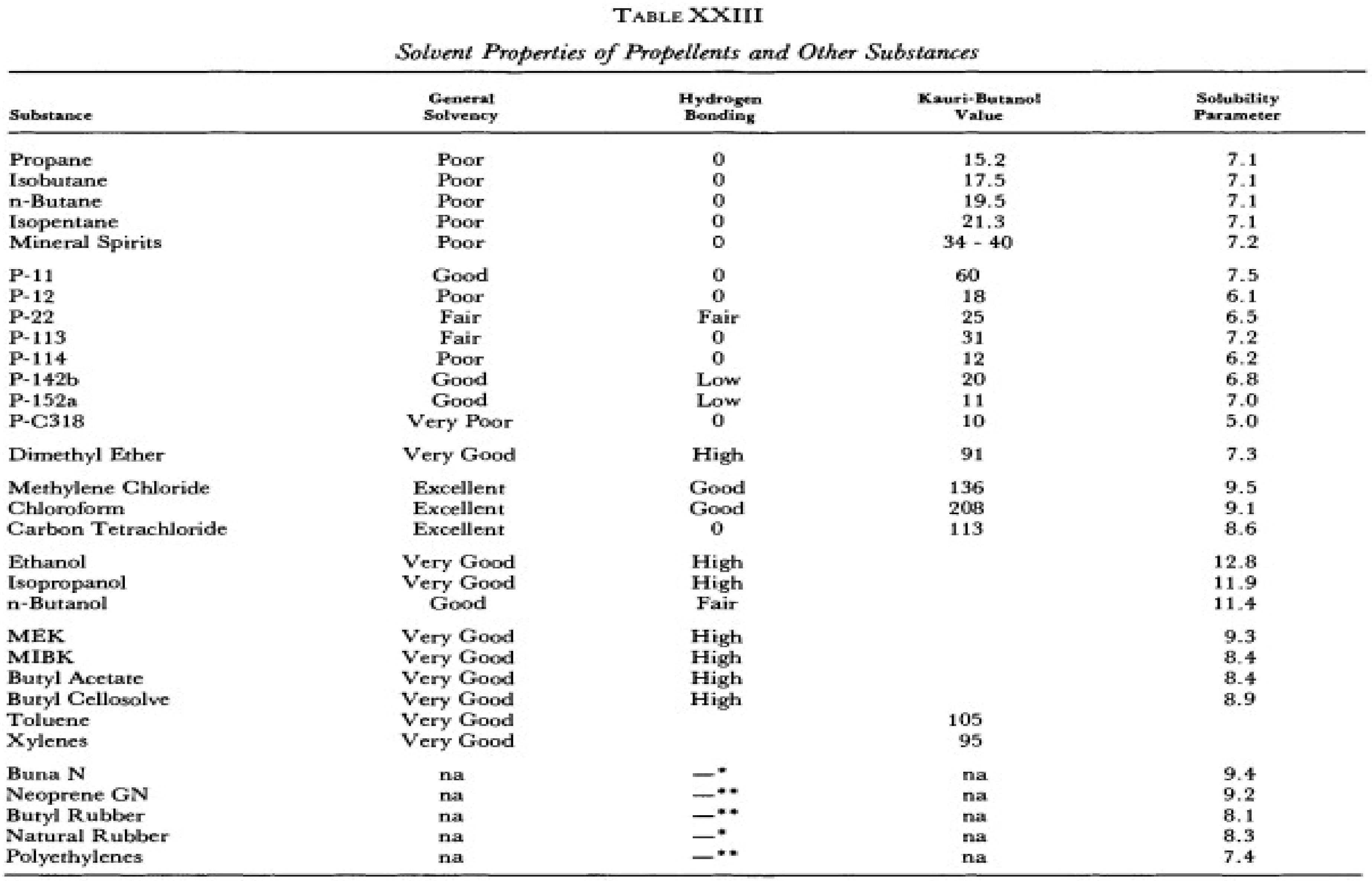

Table XXIII

Solvent Properties of Propellents and Other Substances

Substance	General Solvency	Hydrogen Bonding	Kauri-Butanol Value	Solubility Parameter
Propane	Poor	0	15.2	7.1
Isobutane	Poor	0	17.5	7.1
n-Butane	Poor	0	19.5	7.1
Isopentane	Poor	0	21.3	7.1
Mineral Spirits	Poor	0	34 - 40	7.2
P-11	Good	0	60	7.5
P-12	Poor	0	18	6.1
P-22	Fair	Fair	25	6.5
P-113	Fair	0	31	7.2
P-114	Poor	0	12	6.2
P-142b	Good	Low	20	6.8
P-152a	Good	Low	11	7.0
P-C318	Very Poor	0	10	5.0
Dimethyl Ether	Very Good	High	91	7.3
Methylene Chloride	Excellent	Good	136	9.5
Chloroform	Excellent	Good	208	9.1
Carbon Tetrachloride	Excellent	0	113	8.6
Ethanol	Very Good	High		12.8
Isopropanol	Very Good	High		11.9
n-Butanol	Good	Fair		11.4
MEK	Very Good	High		9.3
MIBK	Very Good	High		8.4
Butyl Acetate	Very Good	High		8.4
Butyl Cellosolve	Very Good	High		8.9
Toluene	Very Good		105	
Xylenes	Very Good		95	
Buna N	na	—*	na	9.4
Neoprene GN	na	—**	na	9.2
Butyl Rubber	na	—**	na	8.1
Natural Rubber	na	—*	na	8.3
Polyethylenes	na	—**	na	7.4

Emulsion Technology

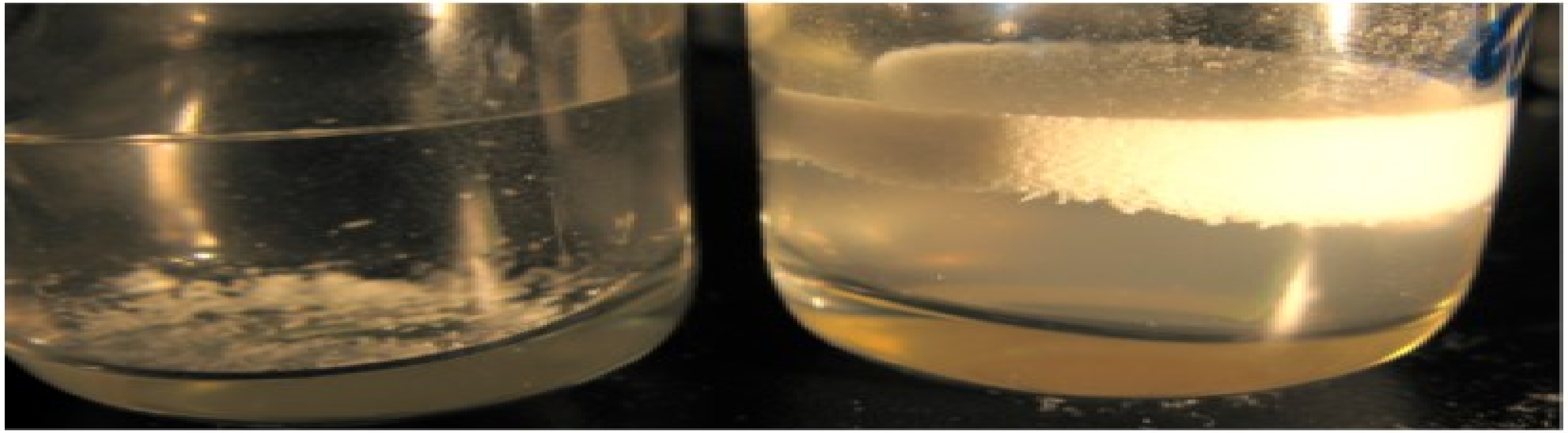

Figure 2. Micronized GP alone (left vial) and micronized GP cosuspended with phospholipid microparticles (right vial) demonstrating formation of drug—microparticle agglomerates.

At ambient temperature, the density of the propellant, 1.206 kg/L, is higher than that of the phospholipid microparticles, 1.066 kg/L, and lower than that of the drug crystals, in this case, glycopyrrolate, 1.372 kg/L; therefore, if the drug and porous particles were not attached to each other in the co-suspension they would separate over time, i.e., the drug crystals would sediment, as shown in the left vial in Figure 2, and the porous particles would cream. However, even when gravitational acceleration was amplified 200-fold by centrifugation, no drug crystals sedimented, but rather rose to the surface together with the phospholipid microparticles, as can be observed in the right vial in Figure 2.

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