

BUSINESS REPORT

SPECIALITY AND HIGH PERFORMANCE RUBBERS

**Nicola Scott and
Vincent Whalley**

rapra

RAPRA

TECHNOLOGY LTD.

Registered Office:
Shawbury Shrewsbury Shropshire
SY4 4NR England
Telephone: Shawbury (0939)250383
Telex 35134 Fax (0939) 251118

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Vincent Whalley**

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1. INTRODUCTION

It is the intention of this report to provide information on a selection of elastomers which are generally acknowledged as being in the 'high performance' category. Because these elastomers provide a combination of properties not found in ordinary synthetic rubbers they are often referred to as 'speciality rubbers'.

In recent years designers have placed increasing emphasis on the need for maintenance-free components whilst innovative design has led towards increases in energy efficiency. Additionally the need for rubber components which are able to withstand more aggressive environments for extended periods of time has stimulated the market for high performance rubbers.

This report is primarily concerned with:

- (i) the materials available and their major characteristics, advantages and limitations;
- (ii) the processes used;
- (iii) the products and end use markets for which the materials are intended, and the key market trends;
- (iv) relevant statistical and economic information, including the manufacturers of the materials and available data on their capacities.

Information was primarily collected from Rapra Technology's database of worldwide literature and directly from the materials manufacturers. Additionally the report takes account of the views of Rapra's experts in rubber technology.

The report is presented in five sections. Section 2 summarises the report. Section 3 describes the various materials, both comparatively and individually. Details of important specialist properties and applications, as well as prices, manufacturers and their capacities are covered in this section. Section 4 describes the main processing routes and some special requirements associated with the individual materials, while Section 5 focuses on the major applications for these elastomers along with overall market sizes and future trends.

2. EXECUTIVE SUMMARY

The first stage in a report of this nature was to identify the elastomers concerned. Detailed discussion with experienced Rapra rubber technologists and a preliminary survey of the literature indicated the ambiguity of the term 'high performance'. With this factor in mind we selected nine generic categories which are representative of these speciality elastomers. They are:

- Acrylic Rubbers
- Epichlorohydrins
- Fluoroelastomers
- Modified Polyethylenes
- Polynorbornenes
- Polysulphides
- Propylene Oxide Copolymers
- Silicone Rubbers
- Thermoplastic polyester/ether elastomers

We have prepared our best estimates of current world market size, which should be regarded as orders of magnitude rather than precise data. With a world consumption in the range 165,000–185,000 tonnes/yr, speciality elastomers represent a mere 1.8% of total world rubber consumption or 3% of synthetic rubber usage. However, when translated into value terms, these proportions increase significantly to 7-8% and 10% respectively.

Silicone rubbers are the most significant, of the above materials, with an estimated world consumption of 60,000 tonnes per year. The second most widely used speciality elastomer is chlorosulphonated polyethylene with an estimated world consumption of 40,000–50,000 tonnes per year. Acrylics, with an annual world consumption figure of 30,000 tonnes, follow in third position. The balance is accounted for by thermoplastic elastomers (15,000 tonnes/yr), epichlorohydrins (10,000–15,000 tonnes/yr), polysulphides (5,000–10,000 tonnes/yr), fluoroelastomers (5,000 tonnes/yr), polynorbornene (1,000–2,000 tonnes/yr) and finally propylene oxides with an annual consumption figure of less than 1,000 tonnes. Chlorinated polyethylene has been omitted from our estimates as available data is entirely inadequate.

Average growth rates of 6-7% per annum are expected in the USA for speciality elastomers up to 1988, and 5% in W. Europe to 1990. Those elastomers which are expected to demonstrate above average growth include fluoroelastomers and thermoplastic polyesters. The more mature materials such as acrylics and polysulphides will, on the other hand, demonstrate growth rates below this average.

The price of these elastomers varies enormously, from £70,000 per tonne for high grade fluorosilicones to £1,500 per tonne for the basic grades of polynorbornene and chlorinated PE. Compared with natural rubber at around £520 per tonne and SBR at around £800 per tonne they are certainly expensive. Nitrile and polychloroprene rubber, on the other hand, are comparable in price to both polynorbornene, chlorinated PE and chlorosulphonated PE.

Speciality elastomers are used in a wide range of different industries. The automotive industry is of particular significance where thermoplastic polyesters, chlorinated polyethylene, fluoroelastomers and acrylics are expected to show sizeable growth at the expense of nitrile rubber, butyl rubber, polychloroprene and styrene butadiene rubber. The electrical industry also utilises these elastomers, although applications tend to be of a

specialised nature, e.g. high voltage, aggressive or high temperature environments.

The excellent weatherability, fire resistance, oil and chemical resistance, or heat ageing associated with some of these elastomers leads to applications in the construction area. Chlorosulphonated and chlorinated polyethylene are widely used in roofing, whilst silicones, acrylics and polysulphides are used as sealants.

Many of these speciality rubbers are used in offshore drilling and chemical plant equipment, where oil resistance, chemical resistance, high temperature resistance, low temperature flexibility and sour gas resistance are among the properties required. Fluoroelastomers, acrylics, epichlorohydrins and chlorosulphonated polyethylene are widely used in applications such as seals, cable sheathing and safety clothing.

Other areas of application include the medical field (silicone rubbers are very important biocompatible materials), domestic appliances (seals and gaskets) and the aerospace industries.

Growing performance demands in the future will ensure growth in the market for speciality elastomers. Competition between the individual materials will continue to be fierce and the exceptionally large price differentials may be lessened in an attempt to make the use of, for example, fluoroelastomers and silicones, more attractive. Speciality elastomers present:

An opportunity for business growth and diversification

A challenge in that they are too important to ignore

3. THE MATERIALS

3.1 General Outline

A synthetic rubber is a material obtained by polymerisation of one or more monomers, possessing the approximate physical properties of Hevea rubber, e.g. at least 100% elongation and rapid elastic recovery.

The speciality rubbers satisfy these conditions whilst also providing special properties such as oil resistance, high temperature resistance, low temperature flexibility and good weatherability. It is the unique combination of properties of these elastomers that has made them increasingly popular. With the exception of the silicones all the elastomers covered in this report are principally organic and their prices are, to varying degrees, affected by the price of oil. In the present climate of falling oil prices, this is a decided advantage.

3.2 Manufacturers and their Capacities

The following tables were compiled using the January 1985 edition of 'Worldwide Rubber Statistics', published by the IISRP, along with a variety of published literature. It should be noted that, with the exception of acrylics, fluoroelastomers and silicones, most of the polymers are made by a very few companies.

Elastomer	Country	Company	Tradename	Plant location	Capacity tonnes/yr	Comments
Acrylic Rubbers and Latexes	France	Protex	Acrylon	Chateaubault	2,000	
	W. Germany	Bayer AG	Acralen	Leverkusen	10,000*	
	Italy	Enichem Elastomeri	Elaprim AR	Rho	500	
	USA	American Cyanamid	Cyanacryl	Bound Brook	4,000	
		B.F. Goodrich	Hycar	Louisville, KY	2,000	
		Reichhold	Tylac	Cheswold, Del.	500	
				Kensington, Ga.		
		Du Pont	Vamac	Orange, Tex.	N.A.	
	Japan	Nippon Zeon	Nipol	Kawasaki	500	
		Mitsui Toatsu	Polylac	Ofuna	2,500*	
		Toa Paint	Acron	Osaka	1,300	
		Takeda	Ultrasol	Hikami	1,500	
Epichlorohydrins	Taiwan	Toa Resin	Acron	Taipei	600	
	USA	Hercules	Herclor	Hattiesburg, Miss.	6,000*	
		B.F. Goodrich	Hydrin	Avon Lake, Ohio	2,500	
	Japan	Nippon Zeon	Gechron	Tokuyama	600*	
Fluoro-elastomers		Osaka Soda	Epichlomer	Mizushima	1,200	
	Italy	Montefluos	Technoflon	Linate	1,000	Manufacturers and capacities of fluorosilicones are included under 'Silicone Rubber'. Du Pont have recently announced further expansion plans which include a joint venture with Showa Denko, Japan. A precompounding plant for Viton, capacity 500 tonnes/yr plant finished product, will be built near Tokyo
	USA	3M	Fluorel/Kel-F	Decatur, Ala.	N.A.	
		Du Pont	Viton	Deepwater, NJ	2,400	
		Du Pont	Kalrez	Wilmington, Del.	N.A.	
		Firestone	PNF	Akron, Ohio	N.A.	
	Japan	Diakin Kogyo	Dai-El	Osaka	700	
		Asahi Glass	Aflas	Chiba	N.A.	
	Belgium	3M	Fluorel	Zwijndrecht	2,000*	
	Netherlands	Du Pont	Viton	Dordrecht	2,000	
Modified poly-ethylenes	W. Germany	Hoechst	Hostapren	—	N.A.	Dow Chemical have recently announced plans to build a 22,000 tonnes/yr plant in Europe for the manufacture of chlorinated polyethylene
	USA	Dow Chemical	CPE Elastomers	Plaquemine, La	45,000*	
		Du Pont	Hypalon	Beaumont, Texas	34,500	
	Japan	Osaka Soda	Daisolac	Amagaski	200	
		Showa Denko	Elaslen	—	3,000	
		Toyo Soda	Toso-CSM	Shinnanyo	2,000	
	Hungary	Barrodi	—	—	N.A.	
	UK	Du Pont	Hypalon	Londonderry, N.I.	N.A.	
Poly-norbornene	France	CdF Chimie	Norsorex	Carling	2,500*	
Polysulphide rubbers	USA	Thiokol	Thiokol SA, FT	Moss point, Miss.	9,100	
	Japan	Toray-Thiokol	LP	Chiba	2,000	
Propylene Oxide Copolymers	USA	Hercules	Parel	Hattiesburg, Miss.	6,000*	

Elastomer	Country	Company	Tradename	Plant location	Capacity tonnes/yr	Comments
Silicone Rubbers	Belgium	Dow Corning	Silastic	Seneffe	N.A.	
	France	Rhone-Poulenc	Rhodorsil	St. Fons	N.A.	
		G.E. Europe	Blensil	Cergy Pontoise	N.A.	
	W. Germany	Bayer	Silopren	Leverkusen	N.A.	
		Wacker Chemie	Wacker Silicones	Burghausen	4,100*	
	Netherlands	G.E. Europe	Blensil	Bergen op Zoom	N.A.	
	UK	Silicone Prod'ts UK	Silpruf Electrisil	Lostock, Bolton, Lancs.	N.A.	
		Dow Corning Ltd.	Silastic	Barry, S.Wales	N.A.	
		J-Sil Silicones	J-Sil	Worsley, Manchester	1,500	
	USA	General Electric	GE Silicone	Waterford, N.Y.	2,700*	
		Mobay Chemicals	Baysilicone	—	N.A.	
		SWS Silicones	SWS Silicone	Adrian, Mich.	N.A.	
		Dow Corning	Silastic	Midland, Mich.	N.A.	
			RTV Silicone	Costa Mesa, Cal.	N.A.	
			FSR Rubber	Elizabethtown, Tenn.	N.A.	
		Union Carbide	Carbide Silicone	Sisterville, W.Va.	622	
		Rhone-Poulenc	Rhodorsil	Lakewood, N.J.	1,400*	
	Argentina	Rotec Tucuman	—	San Miguel de Tucuman	130	
	Brazil	Wacker Quimica	Wacker Silicones	Sao Paulo	N.A.	
	Mexico	Wacker Mexico	Wacker Silicones	—	N.A.	
			Silopren	Santa Clara	N.A.	
	Japan	Toshiba Silicone	TS	Ota	6,000*	
		Toray Silicone	SH	Chiba	6,000*	
		Shinetsu	Ke	Isoke	10,000*	
Thermo-plastic Polyesters/Ethers	Netherlands	Akzo	Arnitel	Emmen	3,000	
	USA	Du Pont	Hytrell	Deepwater, N.J.	7,200	
		General Electric Co.	Lomod	Mt.Vernon, Ind.	N.A.	
	Japan	Toyobo	Pelprene	Iwakuni	2,000*	
		Du Pont/Toyo	Hytrell	Ehime	4,000	
	Luxembourg	Du Pont	Hytrell	Luxembourg	N.A.	

*indicates capacity estimated by press — not supplied by manufacturer

3.3 Comparative Properties

All rubbers have one property in common: elasticity. High performance elastomers have established themselves because they have combinations of properties not found among general purpose rubbers. These might include combinations of some of the following: weatherability, low temperature flexibility, heat resistance, oil resistance and flame resistance.

Rubbers that have good flame resistance are based on halogen-containing polymers. These include chlorinated polyethylene, chlorosulphonated polyethylene and epichlorohydrin rubbers. Rubbers which are resistant to oil, and to some extent liquid fuels, contain polar substituents which give them the necessary resistance to swelling. These include acrylates, polysulphides and fluorocarbons.

Heat resistant rubbers are characterised by a saturated polymer chain or the presence of only a few double bonds. These include silicones, acrylates and fluorocarbons. Good weatherability and ozone resistance are influenced in a similar way, whilst low temperature flexibility is associated with those polymer-chains which remain mobile at low temperatures.

Properties such as weatherability, oil resistance and abrasion resistance are generally described qualitatively, i.e. A = Excellent through to D = Poor. A summary of the comparative properties of most of the elastomers covered in this report is given in Table 3.1. This table has been compiled from manufacturers literature and standard property data.

Figure 3.1 shows heat vs oil resistance, indicating type and class according to the SAE J2000 specification system. Thermoplastic elastomers are not covered by this specification but have been positioned to allow comparison.

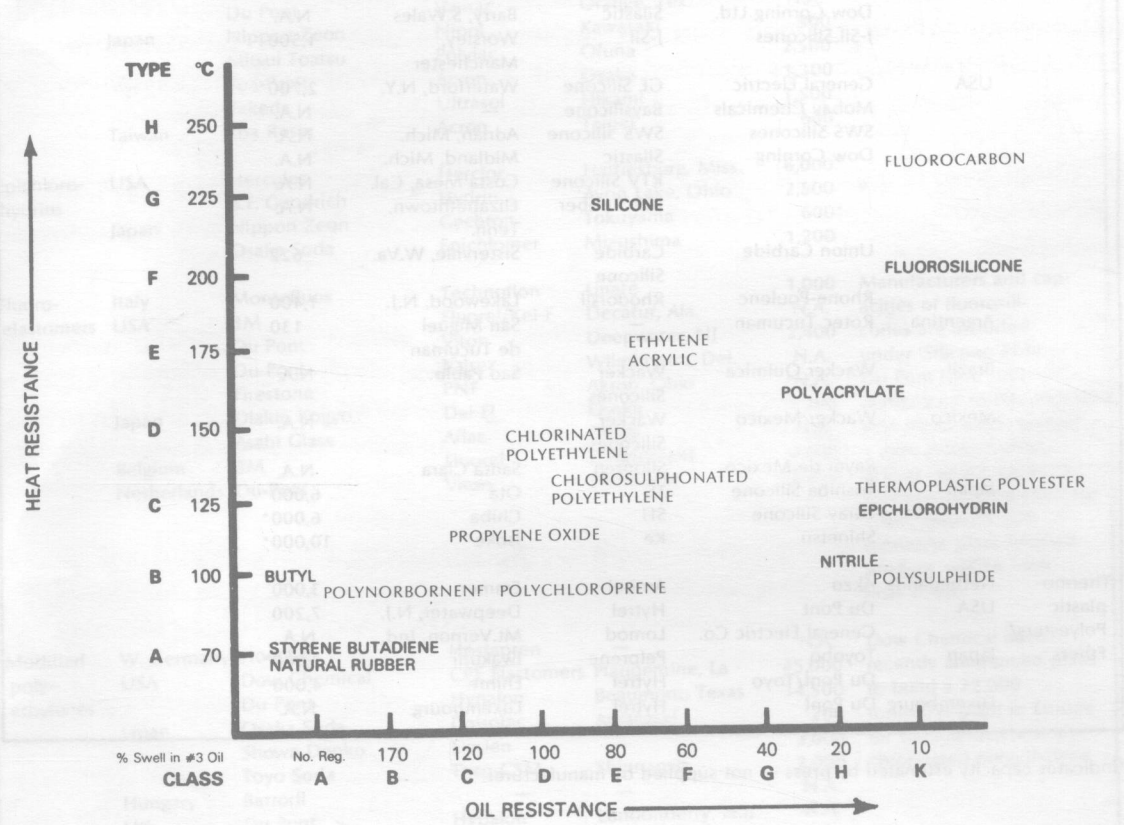


Figure 3.1 Comparison of heat and oil resistance for various elastomers

3.4 Prices

Typical price ranges for the various elastomers are given in Table 3.2. General purpose rubbers and Natural Rubber are included to allow comparison. Estimated free world consumption figures are also included in order to provide an idea of the value of each individual market.

There are no indications, at present, of any major price movements which might significantly perturb the price differentials. There is a plentiful supply of all the main precursors, many of which as already indicated are hydrocarbon based. The price of oil has fallen by some 50% in the past year, and although it is unlikely to rise significantly, some authorities believe that the price is levelling out and may harden significantly by the end of the year.

3.5 Individual Materials and their Variants

3.5.1 Acrylic Rubber

Polyacrylic rubbers are copolymers of monomeric acrylic esters and reactive curesite monomers. The first commercial products were introduced by B.F. Goodrich in 1947.

Table 3.1 Property Comparisons

	FKM	FVMQ	Q	ECO	ACM	CSM	PTR	VAMAC	HYTREL	NORSOREX
Specific gravity	1.4-1.95	1.35-1.65	1.07-1.7	1.36-1.27	1.10	1.12-1.28	1.25-1.34	1.08-1.12	1.2-1.25	1.08-1.15
Temperature service range, °C	-45 to 316	-54 to 232	-100 to 300	-54 to 150	-10 to 150	-23 to 135	-50 to 100	-40 to 170	-70 to 160	-45 to 90
Hardness range (Shore A or D)	45-95A	40-80A	30-85A	40-90A	45-90A	40-95A	20-80A	40-95A	40-72D	10-70A
Tensile strength, MPa (max.)	20	10	10	18	15	17.2	8.96	17.2	44.1	23
Elongation at break, % (max.)	400	500	700	400	400	-	-	-	450	700
Abrasion resistance	B	C	C/D	B/C	B/C	B	D	A/B	A	B
Resistance to:										
Ozone	A	A	A	B/A	A	A	A	A	A	B
Radiation	B	B	B	C	B	A	A	A	A	B
Water	A/B	A	A	B	C/D	B	B/C	B	A	A
Steam	B	B	C/B	C	D	B	D	C	B	A
Concentrated alkali	B	B	B	C	D	A	B	A	B	-
Concentrated acid	A	B/C	C	C	C/D	A	C/D	D	D	C
Alcohol	B	B	B	A	D	A	B	A	A	-
Aliphatic hydrocarbons	A	B	D	B	B/C	B	A	A	A	C
Aromatic hydrocarbons	A	C	D	B/C	D	C	A/B	C	B	D
Lubricating oil	A	A/B	B	A/B	A	B/A	-	B	B/A	B
Key to Material Abbreviation:	<p>A - Excellent B - Good C - Fair D - Poor</p>									
FKM	- fluorocarbons									
FVMQ	- fluorsilicones									
Q	- silicone rubber									
ECO	- epichlorohydrin									
ACM	- acrylates									
CSM	- chlorosulphonated polyethylene									
PTR	- polysulphides									
VAMAC	- ethylene/acrylic rubber									
HYTREL	- thermoplastic polyesters									
NORSOREX	- polynorbornene									

Note: ASTM D1418 Designations have been used where possible, however the tradenames VAMAC, HYTREL and NORSOREX have been used where no official designation exists

Table 3.2 Typical Price Ranges and Estimated World Consumption

	£/kg	World Consumption '000 tonnes, 1985
Fluorosilicones	55.00–70.00	5
Fluorocarbons	22.00–46.00	
Silicones	3.75–18.00	60
Propylene oxide copolymers	3.90– 4.20	<1
Thermoplastic polyesters	3.50– 4.50	15
Acrylics	3.45– 4.45	30
Polysulphides	3.00– 3.70	5–10
Epichlorohydrins	3.00– 3.30	10–15
Chlorosulphonated polyethylene	1.95– 2.75	40–50
Polynorbornene	1.50– 1.79	1–2
Chlorinated polyethylene	1.50– 1.60	–
Nitrile	1.20– 1.50	196*
SBR	0.70– 0.86	2721*
Polychloroprene	0.51– 0.54	4335*
Natural Rubber (RSS1)	2.20– 2.27	254*

*Estimated by the IISRP. SBR figure includes solid and latex rubber

Traditionally acrylic rubbers were based on methyl, ethyl, or other alkyl acrylates. Nowadays a new family of rubbers, Ethylene/Acrylics, are also regarded as acrylic rubbers.

Acrylates (ACM's) are highly resistant to oxygen and ozone, and their heat resistance is superior to that of all other commercial rubbers except the silicones and the fluorine-containing rubbers. ACM's are renowned for their outstanding resistance to hot oils, including those containing sulphur, sulphur-bearing chemicals, and other additives. ACM's are also resistant to most lubricating oils due to their saturated nature. They can be compounded to provide excellent flex life and also have excellent resistance to gas permeability.

The most significant disadvantage associated with ACM's is their poor water resistance. Acrylates are not recommended for use with water, steam or water soluble materials such as methanol or ethylene glycol. Low temperature flexibility is not good and these rubbers decompose in alkaline solutions and are swelled by acids. ACM's are not high strength elastomers. Tensile strength and abrasion resistance are low. They have enjoyed considerable growth in the automotive industry in recent years since, although more expensive than less heat resistant elastomers, they are considerably cheaper than silicones and fluoroelastomers.

Elastomers based on ethylene-acrylate copolymers were introduced in 1975 by Du Pont under the tradename Vamac. This family of elastomers was introduced to provide acrylic rubber with higher strengths, but as a result oil resistance is poorer. Vamac is a terpolymer of ethylene and methyl acrylate with a cure site monomer present. The acrylic segment provides oil resistance whilst the ethylene segment yields good low temperature performance.

Vamac has good heat resistance combined with good resistance to hot oils, hydrocarbon-based or glycol-based proprietary lubricants, transmission fluids and power steering fluids. It is not recommended for use with esters, ketones, highly aromatic fluids or high pressure steam. General service temperature range is -40°C to 170°C . A special feature of

Vamac is its nearly constant damping characteristic over broad ranges of temperature, frequency and amplitude.

Applications for both acrylates and Vamac are similar, Vamac being specified when low temperature flexibility becomes important. Acrylates are used extensively in:

Bearing seals in transmissions	Lip seals
O-rings	Spark plug boots
Gaskets	Valve stem seals
Hose	Belting

Vamac has two main areas of application, automotive and electrical, these include:

Mounts	Hoses
Gaskets	Ignition-wire jackets
Seals	Cable jackets for railways, oil platforms,
Boots	ships and building installations

Details of the manufacturers of both acrylates and ethylene/acrylic rubbers are given in Section 3.2.

3.5.2 Epichlorohydrin

Epichlorohydrin was first manufactured on a commercial basis in 1965 by Hercules. Epichlorohydrin rubber is available as a homopolymer (ASTM designation CO), copolymer (ECO) and more recently as a terpolymer (ETER - not an ASTM designation) which is a copolymer containing a third component having a lateral double bond. Epichlorohydrins contain saturated chains, repeating oxygen atoms (ether linkages) and pendant chlorine atoms. The saturated chain means increased resistance to oxidation, whilst the presence of oxygen atoms increases polarity and therefore contributes solvent resistance to non-polar or hydrocarbon materials. The presence of chlorine atoms also reinforces the polar effects.

Epichlorohydrins are compounded with a variety of materials, which include reinforcing fillers, processing aids, stabilisers, plasticisers and accelerator systems, to produce the final compound/property characteristics. When reinforced, these compounds have moderate tensile strength and elongation properties, plus an unusual combination of other characteristics. One of these is low heat build-up which makes them suitable for applications involving cyclic shock or vibration.

All three epichlorohydrins are high temperature, oil and ozone resistant rubbers. The homopolymer has outstanding resistance to ozone, good resistance to swelling by oils, intermediate heat resistance, extremely low permeability to gases and excellent weathering properties. Disadvantages include low resilience and a low temperature flexibility limit of only -15°C .

The copolymer is more resilient and has low temperature flexibility to -40°C , but it has poorer permeability. Heat resistance and resistance to swelling by oils are comparable to those of the homopolymer.

The terpolymer has oil and fuel resistance comparable with high ACN-NBR type

compounds, low temperature flexibility to -40°C and heat resistance similar to EPDM but inferior to polyacrylates. It also possesses excellent dynamic properties, permeation resistance to gases such as nitrogen and oxygen, and ozone resistance.

Epichlorohydrins are attacked by mineral acids and are swollen by aromatics, chlorinated hydrocarbons and polar fluids. Resistance to alcohols is, however, good.

Epichlorohydrins are generally specified for flexible parts where temperatures may reach 150°C and where oils, greases and fuels may be present. Typical applications are:

Diaphragms	Gaskets
Vibration control equipment	Fuel Hose
Mounts	Rollers
Seals	Belting

The two major manufacturers of epichlorohydrin rubber are Hercules and B.F. Goodrich. Details of plant locations, capacities, tradenames etc. are given in Section 3.2.

3.5.3 Fluoroelastomers

In 1957, the first commercial fluoroelastomers were introduced by Du Pont and 3M. Today fluoroelastomers are used in most industries as they are uniquely capable of withstanding high temperatures in conjunction with aggressive chemicals, fuels and lubricants.

They are notably resistant to swelling in aliphatic, aromatic and chlorinated hydrocarbons, fuels and oils and many other organic liquids. They display good-to-excellent resistance to chemical attack, flame propagation, oxidation, ozone and weathering. Resistance generally increases with increasing fluorine content.

Thermal stability is also an important property, in particular fluorocarbons are unmatched by any other type of elastomer for their performance at elevated temperatures over an extended period of time. Their exceptional resistance to compression set is also important as the largest end-use for fluoroelastomers is in seals. Fluorocarbons have medium tensile strength but fluorosilicones are rated as low tensile strength elastomers. With the exception of Kalrez, a perfluoroelastomer, fluoroelastomers are not recommended for use in polar solvents and caustic ammonia.

Fluoroelastomers are classified either as carbon-carbon chain polymers, heterochain polymers or as polymers with inorganic backbones.

1. Carbon-carbon chain polymers include fluorine containing dienes, polyfluoroalkyl acrylates and those based on co- and ter-polymers of vinylidene fluoride. The latter are easily the most successful of the fluoroelastomers. This class is generally referred to as fluorocarbons. Table 3.3 includes information on their manufacturers and associated tradenames. Fluorocarbons are generally specified over other fluoroelastomers when high temperature resistance is important.

2. Heterochain polymers include polythiocarbonyl fluoride, polyperfluoroalkylenetriazines and nitroso rubber. None of these have ever been manufactured commercially due to their very high cost and the difficulties encountered in production.

3. Polymers containing inorganic backbones include fluorosilicones and fluorinated

polyphosphazenes. These are generally specified when low temperature flexibility and softness are required. Table 3.3 includes information on their manufacturers and associated tradenames.

Table 3.3 Fluorine-containing Elastomer

Type	Temperature-use range, °F, (°C)	Fluorine content, %	Characteristics	Tradename
Fluorocarbon	-51 to 601 (-46 to 316)	53 to 70	Low compression set, high-temperature stability, fuel, oil and chemical resist. S.G. = 1.80 to 1.86	Fluorel
				KEL-F
				Viton
				Kalrez
Fluorosilicone	-65 to 450 (-54 to 232)	30 to 40	Low-temperature flexibility, softness S.G. = 1.35 to 1.65	Technoflon
				DAI-EL
				Aflas
Fluoroalkoxy- phosphazenes	-65 to 450 (-54 to 232)	30 to 40	Low-temperature flexibility, fuel, oil and chemical resistance S.G. = 1.75	Silastic
				FSE
				PNF

Source: Materials Engineering, 94, 1, July 1985

Due to the very wide range of grades of fluoroelastomers available it would be impossible to outline exact applications, however the manufacturers claim that the versatility of the fluoroelastomers allows them to meet the most divergent processing and application requirements.

Major applications include:

O-rings	Fuel cells
V-rings	Electrical connectors
U-rings	Valve tubes and stems
Gaskets	Expansion joints
Shaft seals	Safety clothing and gloves
Hydraulic hose	Stators for pumps
Valve stem seals	Tank linings
Diaphragms for fuel pumps and carburettors	Chimney and duct coatings for high SO ₂ content exhaust gases
Thermoshrinkable tubes for wire insulation	

Details of the major manufacturers and their capacities are given in Section 3.2.

3.5.4 Modified Polyethylenes

There are two modified polyethylenes which fall into the category of speciality elastomers, chlorinated polyethylene and chlorosulphonated polyethylene.

Chlorinated polyethylenes (CPE's) were introduced in the late 1960's by Dow Chemical. Although earlier grades were produced by the chlorination of low density polyethylene nowadays high density polyethylene is used. This introduction of bulky chlorine atoms into the polyethylene structure reduces the tendency of the polymer to crystallise. In practical terms this means that the polymer exhibits rubbery characteristics instead of being rather rigid.

Rubbery CPE's have chlorine contents in the range 25–42% by weight; chlorination to higher levels produces more rigid materials. The presence of relatively large amounts of chlorine means CPE's burn more slowly than many other rubbers. CPE's have excellent heat ageing and ozone resistance, good weathering and low temperature characteristics. They have outstanding chemical resistance and fair resistance to oils; as expected resistance to swelling increases with chlorine content.

CPE's are often compared with plasticised PVC, however they have two important advantages over PVC: their retention of flexibility at low temperatures is better and they do not require plasticisers in their compounding. Their temperature service range is similar to that of chlorosulphonated polyethylenes (CSM's).

Applications include:

- Single ply roofing
- Wire and cable
- Automotive parts

Chlorosulphonated polyethylenes (CSM's) were first introduced in 1951 by Du Pont under the tradename Hypalon. Like CPE's, chlorosulphonation reduces the tendency of the polymer to crystallise which means it exhibits rubbery characteristics. Chlorine contents of 24–43% and sulphur contents of 1–1.5% are most typical. Grades suitable for conventional rubber industry processing are produced from high density linear polyethylenes.

General purpose formulations are heat resistant up to 130°C while more specific compounding can give excellent resistance at 150°C. At the other end of the temperature range, compounds are available with good flexibility at –23°C or, with special compounding, down to –40°C. The negligible degree of unsaturation also ensures outstanding resistance to ozone and weathering.

CSM's can be compounded with conventional rubber fillers which leads to an enhancement of properties such as modulus, tensile strength, tear strength and abrasion resistance. White fillers are widely used in light coloured formulations, calcined clay gives particularly easy processing and very good electrical properties, calcium carbonate imparts excellent heat resistance, plate-like structures (talcs) give good definition and finish to extrusions and hydrated alumina and magnesium hydroxide are used in low smoke emission formulations.

For outdoor applications CSM requires UV stabilisation. Even so it is still considered to be one of the most weather-resistant rubbers currently available, furthermore, it resists discoloration by light. Its resistance to swelling in oils and its general resistance to attack by chemicals are both good. Other advantages include resistance to combustion and good resistance to heat ageing.

CSM is widely used in the wire and cable industry where its 'colour flexibility', electrical

properties and flame resistance are important properties. CSM's are also specified for automotive air-conditioning hoses, owing to their low permeability to water and fluorinated refrigerant. Other applications include:

- Coloured extrudates
- Gaskets
- Industrial roll coverings
- Roofing membranes
- Reservoir and pit linings
- Coatings for tanks, inflated fabric structures, garments etc.

Details of the manufacturers and their capacities are given in Section 3.2.

3.5.5 Polynorbornene

CdF Chimie is the sole producer of polynorbornene through its own special process, although there is no patent on the material. Polynorbornene was launched in 1976 under the tradename Norsorex.

Norbornene is obtained by the addition of ethylene to cyclopentadiene. Polymerisation leads to the formation of Polynorbornene which is classed as a hydrocarbon synthetic rubber. Polynorbornene is unusual amongst hydrocarbon synthetic rubbers in that it is a glassy polymer at room temperature with a glass transition temperature of 35°C.

In order to acquire rubbery properties it is plasticised with a wide variety of aromatic, naphthenic and paraffinic oils. Paraffinic oils give the best resistance to low-temperature stiffening, whereas aromatic oils give the best mechanical properties and resistance to ageing. Blends of the various types of oils can be used in order to give a balance of properties. Polynorbornene can be compounded with large quantities of both oil and filler. The amounts of filler, and their type, determine the level of dissipated energy and consequently the resilience. In general for a given plasticiser, damping increases with increasing filler structure.

Polynorbornene is available in a wide range of hardnesses, from 15 Shore A to 80 Shore A and can be formulated to provide either high or low damping. Mechanical properties vary with hardness; excellent tensile strength can be achieved with products of low hardness. Polynorbornene also has low compression set which means it is suitable for sealing applications. It shows good resistance to oils, certain chemicals and ozone. Further advantages include low cost, compared with most other speciality elastomers, and ease of processing. Polynorbornene's temperature service range is -45°C to 90°C which limits its use for certain high temperature environments.

Polynorbornene is generally specified where high mechanical damping is required. Applications include:

- (1) In the automotive industry:
 - Engine, chassis and body mounts
 - Flexible and vibration damping boots for steering column, handbrake and gear lever
 - Vibration and noise isolators for transmission parts
 - Grommets and diaphragms
 - Insulation seals

- (2) In the electronics industry:
- Damping pads and seals for turntables
 - Drive belts and wheels for tape recorders etc.
 - Loudspeaker membrane frames

Other applications include:

- O-rings
- Sheet rubber packing
- Sealing profiles for buildings and appliances
- Printing roll coverings

Section 3.2 includes details of the manufacturing locations and capacities of CdF Chimie's Norsorex.

3.5.6 Polysulphide Rubbers

Polysulphide rubbers were first introduced by the Thiokol Chemical Corporation in 1928. Originally polysulphide rubber was made from ethylene dichloride and sodium polysulphide. This rubber had extremely high resistance to swelling in hydrocarbon liquids, (due to its high sulphur content of c.84% by weight). However, it was difficult to process, had a bad odour and gave off irritating fumes during processing. Nowadays bis(2-chloroethyl) formal is used instead of ethylene dichloride which results in better low temperature properties, better processing and less odour; however, to obtain these benefits, fuel and oil resistance was reduced.

Basic properties of polysulphide rubbers are determined by the type of chain structure and the number of sulphur atoms in the polysulphide groups. Increased sulphur concentration improves solvent and oil resistance, and also reduces the permeability to gases. The addition of small quantities of ethylene dichloride to the basic formulation results in a linear polymer with no crosslinking which means the rubber has no resistance to compression set. However, the addition of ethylene dichloride raises its upper service temperature from 100°C to 121°C.

Polysulphides are resistant to oxidation, ozone and have good adhesion to a wide range of substrates.

Even though substantial improvements have occurred over the years, polysulphide rubber still has several disadvantages. Odour, poor processability, poor mechanical properties and relatively low heat resistance still cause problems and restrict its use.

Polysulphides are well known for their outstanding oil and solvent resistance, a factor reflected in the end-use applications. These include:

- Rubber rollers for coating and printing
- Hoses for petroleum, aromatic fuels, paints etc.
- Paint-can lid seals
- Gas meter diaphragms
- O-rings
- Cements and putties
- Coatings for gaskets

Details of manufacturing capabilities are given in Section 3.2.