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Rubber materials — Chemical resistance

Matériaux en caoutchouc — Résistance chimique

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0. Introduction

Rubber based materials can be degraded by the action of liquids or gases with which they come into contact. The rate and extent of the attack depends not only on the chemical composition of the rubber polymer and the other compounding ingredients, but also on the chemical nature of the liquid or gas, its concentration, temperature, pressure and duration of contact. The thickness of the rubber must be taken into account since the time of penetration of the swelling fluid is dependent on product dimensions and the bulk of a very thick rubber product may remain unaffected for the whole of the projected service life.

1. Scope

This Technical Report is intended as a guide to the behaviour of rubber materials in contact with chemicals such as aggressive gases and fluids, e g acids, alkalies, water solutions, oils and solvents. The information given in this report is based on practical experience of manufacturers and users of rubber materials. Unless there is prior knowledge or experience of the application, a selection based on the tables should always be confirmed by tests on the proposed compounds using the actual product under the appropriate service conditions. In such tests attention should also be given to the possibility of the rubber material contaminating the liquid or gas.

References

ISO 1817 Vulcanized rubbers - Resistance to liquids - Methods of test

ISO 1629 Rubber and latices-Nomenclature

2. Types of chemical and physical change

The effect of chemicals on rubber can in most cases be referred to one or more of the following categories:

2.1 Physical penetration and absorption of an agent into a rubber material, for instance of isooctane into SBR. This phenomenon causes swelling (Ref A) of the rubber sometimes combined with extraction of soluble material from the rubber. If the absorbed fluid is removed, for instance by drying, most of the physical properties return to their original level. If the antidegradants in the vulcanizate are removed by extraction a loss of ageing resistance may result, if the oil is extracted the rubber will be harder.

2.2 Chemical attack

a) Hydrolysis. This is a chemical reaction between water and the rubber polymer, especially under acid and alkaline conditions, which results in reduction of the physical properties. At the same time swelling could take place but this is not always the case. A typical example is the attack of hot water on polyesterurethanes.

b) Oxidation. All organic materials are more or less sensitive to oxidation. This attack will result in degradation of physical properties. Usually the tensile strength will decrease, but, hardness and elongation can either increase or decrease depending on the rubber and the environment. If liquid oxidizing media are used, oxidation may be combined with swelling. A typical example of the latter is the effect of nitric acid on SBR and NBR. As with most other forms of chemical attack, the rate of oxidation increases with temperature.

c) Specific effects such as those due to reaction with chlorine, bromine, ozone etc. Attack by these chemicals is usually confined to the surface of the rubber.

3. Rubber polymers

The rubber materials considered in this Technical Report are based on the following rubber polymers:

	Used symbol (designations in ISO 1629)
Isoprene rubbers, natural	NR
Butadiene rubbers	BR
Isoprene rubbers, synthetic	IR
Styrene-butadiene rubbers	SBR
Isobutene-isoprene rubbers (butyl rubbers)	IIR
Bromo- or chloro-isobutene-isoprene (halobutyl) rubbers	BIIR/CIIR
Ethylene-propylene-diene terpolymers	EPDM
Ethylene-propylene copolymers	EPM
Nitrile-butadiene rubbers	NBR
Chloroprene rubbers	CR
Chloropolyethylene rubbers	CM
Chlorosulphonyl-polyethylene rubbers	CSM
Acrylate copolymers	ACM
Ethylene-acrylate rubbers	EACM
Ethylene-vinylacetate rubbers	EVM
Epichlorohydrin polymers	CO
Epichlorohydrin copolymers	ECO
Polypropylene oxide rubbers	GPO
Polyester urethane	AU
Polyether urethane	EU
Polysulfide rubbers	T
Silicone rubbers	Q
Fluorinated silicone rubbers	MFQ
Fluorinated rubbers	FKM

4. Chemicals

The chemicals listed in this report are thought to be representative of those coming into contact with rubber, and as far as possible at least one member of each class of commonly used organic chemical has been included. Proprietary materials have not been included except those representative of a particular class of service or industrial fluids.

The classification is for normally technically pure chemicals. The same performance may not necessarily apply to commercial chemicals even of broadly similar composition because of any effects contaminants or minor active constitutentents may have. Several commercial chemicals for example may contain trace quantities of oxidizing agents or pro-oxidants. Detergents make another example. These contain chemically active materials and the type and level will vary from supplier to supplier. It should also be noted that mineral oils and fuels vary appreciably in composition even when supplied to a recognized specification. With an oil, resistance to swelling can vary not only with chemical composition but also with the viscosity of the oil.

Common chemical names are used in this Technical Report.

5. Effect of variations in vulcanizate composition

5.1 General

In this report the classification of chemical resistance is directly related to the rubber types listed in Clause 3. However the information used for the classification relates largely to vulcanized rubber compositions containing such compounding ingredients as fillers, softeners and protective agents. Whilst the type of rubber polymer plays a dominant role in determining resistance to many of the chemicals listed in the table, vulcanization and compounding can have an important effect on behaviour. Within one polymer type there can also be significant differences among grades.

The classes given in table 2 are believed to be representative of each rubber type, but it should be stressed that these classes can be changed by a change in composition.

The classification given in table 2 is based on the properties in a formulation suitable for the particular rubber. Usually a compromise between properties is required for an application and this may affect the level of chemical resistance. Under certain conditions e.g. ozone attack performance may be improved by special additives, the use of which may permit an upgrading in class for some polymers. This report is concerned with the behaviour of rubbers, not their selection. The choice of rubber type (and compound) will depend on many factors other than just chemical resistance.

5.2 Raw rubber variations

There are normally many different grades of each rubber polymer and this can have some influence on the chemical resistance. The following are examples of the effect of the particular grade of polymer on its chemical resistance.

NR: Hard rubber (ebonite) is NR (sometimes SBR) with high sulfur. It has better chemical resistance against certain chemicals for instance chlorine and acids, than normal soft NR.

IR has the same resistance as NR. Solution-polymerized IR and low ash content grades are even more resistant to water absorption.

SBR: Glue-Acid (GA) coagulated SBR has lower water swelling than most other grades. Solution - polymerized SBR and low ash content grades are even more resistant to water absorption.

NBR: The content of acylonitrile (ACN), which can vary from about 20 to about 40 % has a great influence on the swelling of nitrile rubber materials in oils and solvents. With higher ACN the rubber has less swelling in mineral oils and most non-polar solvents, but the opposite effect can be observed with polar solvents.

CSM: The content of chlorine has an influence on the swelling of CSM in oils and solvents. With higher chlorine content the rubber has less swelling in mineral oils and most non-polar solvents, but the opposite effect can be observed with polar solvents.

FKM: Some of the peroxide curable types are more resistant to certain solvents, acids, steam and water.

IIR, EPDM: The chemical resistance within each type is, in general, related to the degree of unsaturation. Brominated IIR has a similar chemical resistance as chlorinated IIR.

Urethane rubber: There are two main types of urethane rubber, ester urethane (AU) and ether urethane (EU). EU has a better resistance to hydrolysis in acids, alkalies and water. On the other hand AU swells less in mineral oils and in many solvents.

5.3 Fillers and plasticizers

Carbon black is generally the preferred filler to obtain chemically resistant rubber but mineral fillers can also be used in most rubbers if colours are required. The swelling of a rubber material in oils and solvents is reduced by increasing the filler content because it is the polymer that swells. Increased filler loading generally increases hardness and too high a filler loading results in a weaker rubber. Urethane rubbers generally are not filled while silicone rubbers are generally filled with silica. Fillers which are reactive for instance in acids should be avoided in all rubber materials when used in such agents. When the content of plasticizer is high in a compound, which sometimes is the case in NBR and EPDM, but also in SBR and CR, much of the plasticizer can be extracted from the compound by water, oils and solvents. Thus the volume of the material can decrease which can cause trouble in the case of seals. Chemically resistant rubber materials consequently should have low content of extractable plasticizers but they are difficult to avoid completely.

5.4 Crosslinking

The crosslinking system can also have influence on degradation of a rubber material. With suitable protective agents present, rubber vulcanized by low sulfur systems (monosulphidic crosslinks), peroxides (carbon-carbon crosslinks) or other systems giving thermally stable crosslinks is more resistant to atmospheric oxidation than rubber crosslinked with conventionally higher levels of sulfur. An example is that butyl rubber cured with resins is much more oxidation resistant at high temperatures than butyl rubber cured with sulfur. The number of crosslinks between the rubber molecules will also have an effect on the swelling in oils, solvents and water. Consequently the swelling will be reduced if the sulfur content in NR, SBR and NBR is increased.

When rubber materials based on CR, CSM and FKM are used in hot water of temperature greater than 50°C, the preferred curing system contains lead. Other curing systems give higher swelling and greater deterioration in acids, hot water and aqueous solutions.

5.5 Antidegradants

Antioxidants are used in such rubbers as NR, IR, SBR, BR, CR and NBR to improve resistance to oxidative ageing. Special types may be required where the rubber is to be exposed to chemicals containing trace quantities of certain metals, such as copper, which might otherwise assist oxidation. Antiozonants are added to the same group of rubbers to provide ozone resistance. The choice of the protective system will depend on the conditions of service. As far as possible antidegradants resistant to extraction by solvents or to leaching by aqueous solutions should be used in rubber coming into repeated contact with liquids.

6. Effect of service conditions

The amount of change which may be tolerated in a rubber material depends to some extent on the application and whether it is static or dynamic. If, for instance, an O-ring is used in a dynamic application the volume swelling or shrinkage has to be much lower than in a static application. Several chemicals will only attack the rubber at its surface, and in the case of ozone a tensile strain must be present for cracking (the main form of degradation with ozone) to occur.

7. Criteria applied for the ranking of chemical resistance

As criteria for the chemical resistance in this Technical Report the degradation of the physical properties and the change of volume are taken and it is presumed that 2 mm thick test pieces are completely submerged in the medium. The data referred to for gases and organic solvents are, as far as possible, based on 4 weeks at 23°C, for oils 14 days at 100°C and for aqueous solutions 4 weeks at 70°C if no other conditions are stated. If no temperature is reported, this is unknown. In many cases no time is reported in the references. When a concentration is listed it is in an aqueous solution.

The materials are divided into four classes. Where a class does not appear in table 2, it is because no information exists. A gap does not infer that a rubber material has poor resistance to a given chemical. For chemicals absorbed by the rubber material, resistance is classified primarily according to the extent of volume swell (column B of Table 1) and this criterion applies as long as the hardness change accompanying the swelling is lower than the change given in column C for the same class. If the hardness decrease is higher than that indicated for a given volume swell the material is classified by hardness change.

For chemicals which do not cause swelling or shrinkage, but the physical properties besides hardness change, the material is classified after the verbal description in column D.

TABLE 1

A	B	C	D
Class	Increase in volume* (if applicable) %	Change in hardness (if applicable) ± IRHD	Effect on physical properties
1	less than 10	max 10	Little or no adverse effect
2	10 to less than 30	max 20	Minor effect
3	30-60	max 30	Moderate effect
4	over 60	over 30	Severe effect

* Note - Contact with some chemicals may cause some rubber vulcanizates to shrink; for some applications this is unacceptable and it may be necessary to include specific requirements in product specifications to cover this point.

In the classification the rate of diffusion of gases or liquids into the rubber material has not been taken into consideration. Sufficient time should be allowed for diffusion before effects on swelling and property deterioration are examined.

8. Chemical resistance of rubber materials

The classification of the rubber materials is shown in table 2 and is made on the basis of the references given in the appendix. It is presumed that a suitable compound of the polymer is used.

APPENDIX

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