
Rubber materials — Chemical resistance

Matériaux en caoutchouc — Résistance chimique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 7620 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 4, *Products (other than hoses)*.

This second edition cancels and replaces the first edition (ISO/TR 7620:1986), which has been technically revised.

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Introduction

A wide range of rubber products are used in contact with liquids and other chemicals, in some cases throughout their service life, and thus require suitably resistant rubber formulations. Rubber hoses are used to convey a range of fluids from hot water to fuels, conveyor belting may have to carry aggressive slurries, seals and gaskets are installed to prevent leakage of gases and liquids, rubber-covered rollers manipulate webs as diverse as printing inks, paper pulp and textiles, and rubber-lined tanks are used to store industrial chemicals, including corrosive alkalis and acids, for prolonged periods without risk of contamination. Other products, ranging from tyres to flexible roofing membranes, are exposed to rainfall and atmospheric pollutants.

It is essential a suitably resistant rubber be used because contact with a chemical, whether in the form of a liquid or gas, can lead to deterioration of properties through swelling, extraction of additives and polymer degradation. The rate and extent of such attack depends not only on the chemical composition of the rubber polymer and other compounding ingredients but also on the nature of the liquid or gas, its concentration, temperature, pressure and the 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.

This document has been prepared to assist the selection or evaluation of rubber for chemical resistance. It includes an extensive classification of resistance based on information in over 20 sources and involving about 400 chemicals and up to 25 types of rubber.

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Rubber materials — Chemical resistance

1 Scope

This Technical Report describes a classification system for the reporting and tabulation of the chemical resistance of rubber materials. It also provides guidance on the testing and evaluation of rubber with particular reference to test chemicals described in a number of ISO standards.

This document gives guidance on the behaviour of rubber in contact with chemicals such as aggressive gases and fluids, e.g. acids, alkalis, aqueous solutions, oil and solvents.

The information given in this document is based on the 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 rubber 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.

2 Types of chemical and physical change

2.1 Physical penetration

Physical penetration and absorption of an agent into a rubber material, for instance of isooctane into SBR, may occur. These phenomena cause swelling 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 rubber are extracted, a loss in ageing resistance may result. If extender oil or plasticizer is extracted in quantity, the rubber will harden and shrink.

Gases may penetrate throughout the thickness of thin-walled products without any swelling or damage to the rubber. Gas permeability falls outside the scope of this document but may need to be considered when selecting a rubber material.

2.2 Chemical attack

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

- a) **Hydrolysis.** This is a chemical reaction between water and the rubber polymer, especially under acid and alkaline conditions, which results in degradation of 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 polyester urethanes.
- b) **Oxidation.** All organic materials are more or less sensitive to oxidation. The oxidation is often associated with chemical and thermal processes. This attack will result in degradation of physical properties. Usually, the tensile strength will decrease, but hardness and elongation at break can either increase or decrease depending on the rubber type 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.

NOTE Thermal or thermal-oxidative ageing may be the main consequence of exposure to some chemically inert fluids at high temperatures.

- c) **Specific effects.** Examples are those due to reaction with chlorine, bromine, ozone, etc. Attack by these chemicals is usually confined to the surface of the rubber, but can become progressively deeper with time. Hardened surfaces can crack due to thermal or physical movement.

3 Rubber polymers

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

| Rubber polymer | Symbol |
|--|-----------|
| Natural rubber | NR |
| Butadiene rubber | BR |
| Isoprene rubber | IR |
| Styrene-butadiene rubber | SBR |
| Isobutene-isoprene rubber (butyl rubber) | IIR |
| Bromo- or chloro-isobutene-isoprene (halobutyl) rubber | BIIR/CIIR |
| Ethylene-propylene-diene rubber (terpolymer) | EPDM |
| Ethylene-propylene rubber (copolymer) | EPM |
| Acrylonitrile-butadiene rubber | NBR |
| Hydrogenated acrylonitrile-butadiene rubber | HNBR |
| Chloroprene rubber | CR |
| Chloropolyethylene rubber | CM |
| Chlorosulfonyl-polyethylene rubber | CSM |
| Acrylate rubber (copolymer) | ACM |
| Ethylene-acrylate rubber (ethylene acrylic rubber) | AEM |
| Ethylene-vinylacetate rubber | EVM |
| Epichlorohydrin rubber (homopolymer) | CO |
| Epichlorohydrin rubber (copolymer) | ECO |
| Polyester urethane rubber | AU |
| Polyether urethane rubber | EU |
| Polysulfide rubber | T |
| Silicone rubber | MQ |
| Fluorinated silicone rubber | FMQ |
| Fluorinated rubber | FKM |

About half of the rubbers in the list are marketed as “oil-resistant”. Care should be exercised when using this term for chemical resistance because “oil-resistant” is usually defined in terms of resistance to swelling by mineral oils (or, in test terms, to swelling in one of the ISO 1817 reference oils). It should be appreciated that a rubber resistant to such oils is not necessarily resistant to oils of other types.

It must also be observed that the classification of chemical resistance is also directly dependent on the compounding variations (see Annex A).

Thermoplastic rubbers have not been included because of insufficient experience and test data. Consult suppliers for information on chemical resistance.

4 Chemicals

The chemicals listed in this document are thought to be representative of those coming into contact with rubber, and as far as possible at least one member or 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 normal technically pure chemicals. The same performance may not necessarily apply to commercial chemicals even of broadly similar composition because of any effect contaminants or minor active constituents may have. Several commercial chemicals for example may contain trace quantities of oxidizing agents or pro-oxidants. Detergents provide 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. The chemical composition governs the extent to which a rubber can swell, whereas the oil viscosity governs the rate of penetration into the rubber. A viscous oil diffuses more slowly than a less viscous one.

Common chemical names are used in this document.

5 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 permissible volume change 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. The service temperature is also important because an increase will normally raise the rate of penetration of a fluid and raise the level of swelling.

6 Criteria applied for the ranking of chemical resistance

As criteria for the chemical resistance in this document the degradation of the physical properties and the change in volume are taken, and it is presumed that standard 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 and therefore caution must be exercised when assessing the level of resistance. In many cases, no time is reported in the references. When a concentration is listed, it is in aqueous solution.

Resistance is divided into four classes as defined in Table 1. 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, shrinkage or a significant hardness change, the material is classified in terms of the effect on other properties using the descriptions in column D of Table 1. These properties will include tensile stress/strain characteristics, especially in the case of chemicals able to penetrate into the bulk of the rubber, and surface changes such as crack appearance, crazing, erosion and discoloration in the case of chemicals attacking at the rubber surface.

The descriptions used in column D should not be regarded as being equivalent to the changes given in columns B and C. For most applications, a change in hardness as large as 20 IRHD will be considered much more than a "minor effect", regardless of its importance to product service.

Table 1 — Classification of chemical resistance

| A | B | C | D |
|--------------|---|---|--------------------------------------|
| Grade | Change in volume ^a (if applicable), % | Change in hardness (if applicable), IRHD | Effect on physical properties |
| 1 | Less than 10 | Max. 10 | No significant effect |
| 2 | 10 to 30 | Max. 20 | Minor effect |
| 3 | 30 to 60 | Max. 30 | Moderate effect |
| 4 | More than 60 | Above 30 | Severe effect |

^a 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.

7 Chemical resistance of rubber materials

The classification of the rubber materials in accordance with Clause 6 is shown in Table 3 and is made on the basis of the references listed in Annex C. The appropriate references for each chemical are listed in the right-hand column in the table. It is presumed that a suitable compound of the polymer is used.

The assignment of class 1 rating will not necessarily mean that a rubber is suitable for a given application. The exposure conditions may be more severe than those referred to in Table 3. Other considerations affecting the choice of rubber will include the following:

- processing and manufacturing;
- the specified levels of physical properties;
- the size of the product;
- regulatory requirements, e.g. for foodstuff or water contact.

Where a class does not appear in Table 3, it is because no reliable information exists. An omission does not infer that a rubber material has poor resistance to a given chemical.

Care should be taken when selecting rubber coming into contact with more than one chemical. The classifications given in Table 3 may not be comparable because of differences in exposure conditions (e.g. temperature) and in the formulations used. Note that mixtures of some chemicals can be more aggressive than the individual components.

The classes of chemical resistance have been distilled from a large number of reputable sources in order to obtain a representative result. Nonetheless, it will be appreciated that discrepancies among similar rubber types and related chemicals can still arise because of differences in exposure conditions and the rubber formulation.

8 Methods for the evaluation of chemical resistance

8.1 General

This clause gives guidance on the evaluation of chemical resistance, with particular reference to the standard ISO test methods available for contact with chemicals, fluids and gases.

This guidance is intended for organizations and laboratories wishing to

- a) evaluate the resistance of a specific rubber formulation to one of the chemicals listed in Table 3;
- b) evaluate the resistance of a rubber to a chemical under particular exposure conditions (e.g. temperature or concentration);
- c) use a suitable test rubber for the evaluation of the behaviour of a chemical not listed in Table 3.

Use of appropriate standard test procedures, reference materials and test chemicals will enable comparisons of resistance to be made and reduce differences caused by variations in rubber compound, test conditions and the composition of a chemical.

8.2 Test methods

Essentially, four types of standard test are available:

- 1) *Standard methods for resistance to liquids.*

The most appropriate for rubber is ISO 1817. The equivalent for plastics is ISO 175.

- 2) *Standard methods for resistance to gases.*

These include the following:

- ISO 188 for resistance to air oxygen under conditions that cause oxidative ageing;
- ISO 1431 for resistance to ozone attack, under static or dynamic test strain and under accelerated test conditions;
- ISO 4665 for resistance to weathering involving oxidative ageing, ozone attack and exposure to light with or without water spray.

- 3) *Standard methods for permeation of fluids.*

These include the following:

- ISO 2782 for gas permeability;
- ISO 6179 for the rate of transmission of volatile liquids.

NOTE These last two standards are not intended to determine chemical resistance but are relevant when determining the suitability of a rubber type or rubber formulation for applications such as thin membranes. A chemically resistant rubber may not necessarily be the best choice for resistance to permeation and thus additional measurements are needed to ascertain suitability.

- 4) *Standard methods for product testing.*

Specific tests for determining chemical resistance are described in some methods for finished products, including rubber hoses, footwear, coated fabrics, rubber thread and rubber gloves. For the evaluation of a rubber or rubber formulation, these methods may specify test conditions that are directly relevant to the service environment of the intended product.

8.3 Test chemicals

The test chemical for the evaluation of a rubber is selected in one of two ways:

- 1) *Use of the chemical used in service.*

By definition, adopting the service chemical will ensure the closest match with behaviour in service as long as the test conditions that could influence chemical resistance are comparable. The shortcomings of this approach are that the composition and purity of the service chemical may vary from source to source and from site to site, resulting in a range of test results. Some service fluids may also be unsuitable for laboratory testing.

- 2) *Use of a reference chemical.*

The advantage of using a reference chemical is that composition is constant and so test results can be compared from one laboratory to another. Thus this approach is suitable for material specifications, the assembly of information for a chemical-resistance database, and determining the effect of variations in rubber compounding. The obvious shortcoming is that a reference chemical may not reflect variations in service chemicals that could change the order of chemical resistance.

The best-known reference chemicals in the rubber industry are the test fluids given in ISO 1817. However, many other internationally accepted test liquids and gases are available to the rubber compounder and user as shown in Table 2. Some of the standards listed in the table specify appropriate test procedures for evaluation.

8.4 Rubber formulation

The rubber formulation for evaluating chemical resistance is also selected in one of two ways:

- 1) *Use of the rubber intended for the application.*

This will ensure the closest match with service performance as long as factors such as product thickness and temperature are taken into account. Once again the main shortcoming is that the data may be so specific to the formulation that it cannot be applied to another one.

- 2) *Use of a standard or reference formulation.*

The advantages of using a "standard" rubber formulation are that comparisons can be made between test data from different laboratories, the behaviour of one chemical can be compared with that of another, and comparative information can be added to a chemical-resistance database. An agreed reference formulation can also be designed to ensure reproducible properties, not least those that might influence chemical resistance, e.g. swelling, and to avoid additives that might cause anomalous results or mask the effect the chemical has on the rubber.

The reference formulation may be one developed in-house by the rubber supplier or manufacturer or one taken from an appropriate national or ISO standard.

NOTE The formulations for standard reference elastomers given in ISO 13226 may be suitable for some evaluation work as they have been designed to characterize the effects of liquids on vulcanized rubbers.

The information given in Annex A should assist the development of suitable formulations for reference use. Thus attention is drawn to the effects of plasticizers and oils, crosslinking and antidegradants. Test formulations should be representative but should be as simple as possible to ensure consistency and freedom from unexpected changes such as leaching of oils.