



Plastics — Phenolic resins — Basis for classification

Plastiques — Résines phénoliques — Définitions pour classification

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The reasons which led to the decision to publish this document in the form of a Technical Report type 2 are explained in the Introduction.

0 Introduction

This Technical Report gives an overview of the different types of phenolic resin used in the manufacture of thermosetting plastics. It includes brief descriptions of these resins and other pertinent information, and adds to the definitions given in the related International Standard ISO 472.

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1 Scope and field of application

1.1 This Technical Report defines terms relating to the chemical structure of phenolic resins, their physical state and their degree of condensation and polycondensation, for classification purposes in the manufacture and processing of these resins.

1.2 The definitions apply to all fields of application of phenolic resins in plastics. (See also related definitions in ISO 472.)

2 Reference

ISO 472, *Plastics — Vocabulary*.

3 Basis for classification

3.1 The term “phenolic resins” as used in this Technical Report refers to

- a) synthetic resins or modified products obtained by condensation of phenol with aldehydes, particularly formaldehyde;
- b) products of the addition of phenols to unsaturated compounds (for example acetylene, terpenes and natural resins).¹⁾

NOTE — Resins in which the original properties are so changed by the modification (for example by rosin) that they resemble more closely those of the modifying medium are not regarded as phenolic resins.

3.2 Phenolic resins may be classified in a number of ways, such as by

- a) the type of raw material (see clause 4);
- b) the type of resin produced (see clause 5);
- c) the type of modifying agent (see 5.2);
- d) the physical form of the commercial product (see clause 6);
- e) the degree of condensation (see clause 7);
- f) the type of catalyst (see 8.1 and 8.2);
- g) the type of hardener (see 8.2).

4 Raw materials

4.1 Phenols

Besides unsubstituted phenol, derivatives of phenol used for the manufacture of phenolic resins include cresols, xylenols and other alkylphenols (for example *p-tert*-butylphenol, *p-tert*-octylphenol and *p-tert*-nonylphenol), arylphenols (for example phenylphenol and naphthols) and divalent phenols (such as resorcinol and bisphenol A).

4.2 Aldehydes

The most important aldehyde component is formaldehyde, which is used in various forms, including aqueous solution and solid paraformaldehyde, and also as compounds which give rise to formaldehyde. Other aldehydes (for example acetaldehyde, acrolein, benzaldehyde and furfural) are employed to a more limited extent, as also are ketones.

5 Types of phenolic resin

5.1 Unmodified phenolic resins

Unmodified phenolic resins are produced by condensation reactions of phenols with an aldehyde. Depending on factors such as the volume and molar ratio of the raw materials, the reaction conditions and the catalysts employed, two different classes of product are obtained: novolaks and resols.

1) Strictly speaking, these resins are not what are normally regarded as resins for the production of plastics. They are used particularly in certain surface coatings.

5.1.1 Novolaks (two steps)

Novolaks are non-self-curing, soluble, fusible phenolic resins that remain stable when stored, the phenol nuclei of which are linked primarily by methylene bridges. Novolaks can be made to react further and crosslink by the addition of hardeners (see 8.2); heating is also usually necessary.

See also *novolak* in ISO 472.

5.1.2 Resols (one step)

Resols are soluble, fusible phenolic resins which, in contrast to novolaks, contain methylol groups and methylene-ether and sometimes also methylene-amine bridges. Resols are self-curing; they crosslink into insoluble products when heated and/or mixed with catalysts, without addition of further reaction components. Resols are perishable and can be stored for a limited time only.

See also *resol* in ISO 472.

5.2 Modified phenolic resins

Phenolic resins can be modified by chemical reaction of the methylol or the phenolic hydroxyl groups and/or by physical dispersion of the modifying agent. Such modified phenolic resins can be either self-curing or non-self-curing, depending on their structure.

5.3 Phenolic addition resins

Phenolic resins can also be produced without condensation with formaldehyde by reaction of phenol with unsaturated hydrocarbons. Examples of these are phenol/acetylene and phenol/terpene resins, which are not always self-curing.¹⁾

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6 Forms of commercial product

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Phenolic resins are manufactured and used in various forms, such as

- a) liquids;
- b) solids, as pelletized, flake, granular or finely powdered products;
- c) solutions or dispersions in water and/or organic solvents.

A so-called "aqueous solution" (it is not a real aqueous solution) is one that has a water content of more than 5 % (*m/m*) and an organic solvent content of less than 5 % (*m/m*). (Free phenol is not counted as organic solvent.)

A solvent-containing phenolic resin solution is one that has more than 5 % (*m/m*) of organic solvents.

7 Degree of condensation

Phenolic resins can be crosslinked by the use of heat and/or hardeners and/or catalysts. They pass through the following transitional stages of condensation:

- A-stage: Starting state (*resol* or *novolak*); liquid or fusible, and soluble in alcohol and acetone;
- B-stage: Intermediate state (*resitol*); infusible, but still mouldable with heat and capable of swelling in alcohol or acetone;
- C-stage: Final state (*resite*); infusible and insoluble in alcohol or acetone.

See also *A-stage*; *B-stage*; *C-stage*; *resite*; *resitol* in ISO 472.

1) See footnote on preceding page.

8 Catalysts and hardeners

8.1 Catalysts

Catalysts accelerate the crosslinking reaction. Both acid and basic compounds are suitable for this purpose.

8.2 Hardeners (crosslinking agents)

Formaldehyde, or compounds that release formaldehyde, for example hexamethylenetetramine (hexamine), can be used as hardeners. Resols and isocyanates can also be used as hardeners. Hardeners are generally added only to non-self-curing phenolic resins and cure by chemical reaction (three-dimensional crosslinking).

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