Chemicals used for treatment of water intended for human consumption — Modified starches

ICS 13.060.20; 71.100.80

National foreword

This British Standard is the UK implementation of EN 1406:2009. It supersedes BS EN 1406:1998 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee CII/59, Chemicals for drinking water treatment.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Chemicals used for treatment of water intended for human consumption - Modified starches

Produits chimiques utilisés pour le traitement de l'eau destinée à la consommation humaine - Amidon modifié

Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch - Modifizierte Stärke

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Foreword

This document (EN 1406:2009) has been prepared by Technical Committee CEN/TC 164 “Water supply”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2010, and conflicting national standards shall be withdrawn at the latest by February 2010.

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

This document supersedes EN 1406:1998.

Annex A is informative and gives some information on origin, use and handling of modified starches.

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Introduction

In respect of potential adverse effects on the quality of water intended for human consumption, caused by the product covered by this standard:

1) This standard provides no information as to whether the product may be used without restriction in any of the Member States of the EU or EFTA;

2) It should be noted that, while awaiting the adoption of verifiable European criteria, existing national regulations concerning the use and/or the characteristics of this product remain in force.

NOTE Conformity with this standard does not confer or imply acceptance or approval of the product in any of the Member States of the EU or EFTA. The use of the product covered by this European Standard is subject to regulation or control by National Authorities.

1 Scope

This European Standard is applicable to modified starches used for treatment of water intended for human consumption. It describes the characteristics of modified starches and specifies the requirements and the corresponding test methods for modified starches.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987).*

ISO 1666, *Starch — Determination of moisture content — Oven-drying method.*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling.*

ISO 5377, *Starch hydrolysis products — Determination of reducing power and dextrose equivalent — Lane and Eynon constant titre method.*

ISO 6206, *Chemical products for industrial use — Sampling — Vocabulary.*

ISO 8213, *Chemical products for industrial use — Sampling techniques — Solid chemical products in the form of particles varying from powders to coarse lumps.*

3 Description

3.1 Identification

3.1.1 Chemical names

Chemical names of typical modified starches are listed:

a) non-ionic starch: poly-D-glucose;

b) cationic starch: starch 2-hydroxy-3-(trimethylamino) propylether, chloride;

c) anionic starch: starch carboxymethyl ether, sodium salt.

Other modified starches may be used.

3.1.2 Synonyms or common names

a) starch;

b) modified starch;

c) starch flocculants.

3.1.3 Relative molecular mass

Undegraded potato starch derivatives: typically in the range of 10^6 to 10^8.

3.1.4 Empirical formulae

Empirical formulae for typical modified starches are:

a) non-ionic starch: $(C_6H_{10}O_5)\ n$;

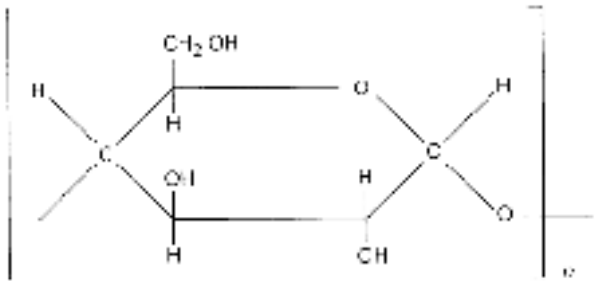
b) cationic starch: $[(C_6H_{10}O_5)(C_{12}H_{24}ONCl)_{0,035\text{-}0,7}]_{n'}$;

c) anionic starch: $[(C_6H_{10}O_5)\ (C_8H_{11}O_7Na)\ 0,113]\ n''$.

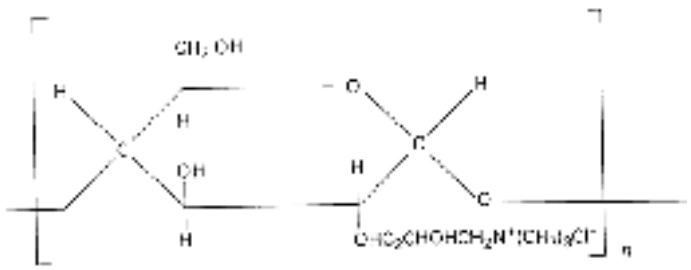
3.1.5 Chemical formulae

Chemical formulae for typical modified starches are:

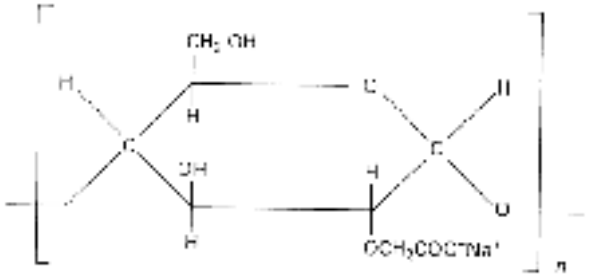
Non-ionic starch:



Cationic starch:



Anionic starch:



3.1.6 CAS Registry Numbers[1)]

a) non-ionic starch: 9005-25-8;

b) cationic starch: 56780-58-6;

c) anionic starch: 9063-38-1.

3.1.7 EINECS reference[2)]

Non-ionic starch has the following EINECS number: 232-679-6.

Modified starches are exempt from EINECS registration providing the reactants used to carry out the modification are EINECS registered.

3.2 Commercial form

Modified starches as specified in this standard are available as solids containing a small amount of residual moisture or as aqueous solutions.

3.3 Physical properties

3.3.1 Appearance

Modified starches are white to pale yellow solids in the form of granule, flake or powder or white to yellowish viscous aqueous solutions.

3.3.2 Density

The bulk densities are as follows:

a) starch powders: 0,4 – 0,7 kg/dm^3;

b) aqueous solution: 1,0 – 1,2 kg/dm^3.

3.3.3 Solubility

The products are soluble in hot or cold water. Their solubility is limited only by viscosity. Typically, anionic starch is soluble to a concentration of 6 % mass fraction, cationic starch to 8 % mass fraction and non-ionic starch to 13 % mass fraction, all in cold water.

3.3.4 Vapour pressure

Not applicable.

3.3.5 Boiling point at 100 kPa

Not applicable.

3.3.6 Melting point

Not applicable.

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1) Chemical Abstracts Service Registry Number.

2) European Inventory of Existing Commercial Chemical Substances.

3.3.7 Specific heat

Not applicable.

3.3.8 Viscosity, dynamic

Not applicable.

3.3.9 Critical temperature

Not applicable.

3.3.10 Critical pressure

Not applicable.

3.3.11 Physical hardness

Not applicable.

3.4 Chemical properties

Starch and starch derivatives are non-hazardous materials and not intrinsically reactive. However, in common with many other organic compounds, a strong exothermic reaction will occur if they are brought into contact in the dry state with a strong oxidizing agent or strong acid.

NOTE In dilute solution, there can be a reaction with, or destruction by, some of the disinfection and oxidizing agents used in water treatment.

4 Purity criteria

4.1 General

This European Standard specifies the minimum purity requirements for modified starches used for the treatment of water intended for human consumption. Limits are given for impurities commonly present in the product. Depending on the raw material and the manufacturing process other impurities may be present and, if so, this shall be notified to the user and when necessary to relevant authorities.

NOTE Users of this product should check the national regulations in order to clarify whether it is of appropriate purity for treatment of water intended for human consumption, taking into account raw water quality, required dosage, contents of other impurities and additives used in the product not stated in the product standard.

Limits have been given for impurities and chemicals parameters where these are likely to be present in significant quantities from the current production process and raw materials. If the production process or raw materials lead to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

4.2 Composition of commercial product

The following requirements shall apply to modified starch products (this specification applies to dry starch):

a) starch content: 86,4 % mass fraction to 92 % mass fraction;

b) moisture content: 6,5 % mass fraction to 12 % mass fraction;

c) extraneous matter: none.

For aqueous solutions of starch:

d) starch content: 50 % mass fraction to 5 % mass fraction;

e) the moisture content: 50 % mass fraction to 95 % mass fraction.

4.3 Impurities and main by-products

Based on the raw materials and manufacturing process (see A.1) there are no significant concentration of additional reactants or by-products which are relevant to the application of this product in drinking water treatment.

4.4 Chemical Parameters

NOTE For the purpose of this standard, “chemical parameters” are those defined in the EU Directive 98/83/EC of 3 November 1998 [1].

Chemical parameters as defined above are not relevant at a reference dose of 5 mg/l.

5 Test methods

5.1 Sampling

Sampling shall be in accordance with ISO 8213 and the recommendations given in ISO 3165 and ISO 6206 shall be followed.

A representative sample of the solid product or aqueous solution, of sufficient mass, shall be obtained immediately after manufacture or from a newly opened package(s). The sample shall be clearly labelled with product name/code, batch number, type of container(s) sampled and date sampled. Reference samples shall be retained for the storage life of the product as claimed by the manufacturer/supplier.

5.2 Analyses

5.2.1 General

Unless otherwise specified, all reagents shall be of recognized analytical grade. The water used shall conform to grade 2 specified in EN ISO 3696.

5.2.2 Main product

5.2.2.1 Determination of starch content

5.2.2.1.1 Principle

The test sample is first heated with dilute hydrochloric acid to convert it by hydrolysis to reducing sugars [2]. Then the dextrose equivalent of the test sample is determined by titrating with the solution thus formed a prescribed volume of mixed Fehling's solution under specified conditions using methylene blue as internal indicator.

5.2.2.1.2 Reagents

5.2.2.1.2.1 Hydrochloric acid concentrated density, ρ = 1,19 g/ml.

5.2.2.1.2.2 Potassium hydroxide, solution at 10 g/l.

5.2.2.1.2.3 Decolourising charcoal.

5.2.2.1.3 Apparatus

Ordinary laboratory apparatus and glassware together with the following:

5.2.2.1.3.1 Conical flask, 250 ml, with glass stopper fitted with reflux condenser.

5.2.2.1.3.2 Volumetric flask, 200 ml.

5.2.2.1.4 Procedure

5.2.2.1.4.1 Test portion

Weigh, to the nearest 0,1 mg, 1 g of test sample into a 250 ml flask (5.2.2.1.3.1).

5.2.2.1.4.2 Determination

5.2.2.1.4.2.1 Hydrolysis of sample

To the flask fitted with reflux condenser (5.2.2.1.3.1) containing the test portion add 100 ml of water and 2 ml of hydrochloric acid (5.2.2.1.2.1). Bring to the boil and reflux for 3 h.

Transfer the contents of the flask and rinsings to a 200 ml volumetric flask (5.2.2.1.3.2). Cool and nearly neutralise with potassium hydroxide solution (5.2.2.1.2.2). Add water to 200 ml and filter through a little decolourising charcoal (5.2.2.1.2.3).

Carry out the above procedure in triplicate to provide sufficient test solution for the titration phase (5.2.2.1.4.2.2).

5.2.2.1.4.2.2 Determination of dextrose equivalent

Determine the dextrose equivalent in accordance with ISO 5377.

NOTE The dextrose equivalent expressed as the number of grams of anhydrous D-glucose per 100 g of the dry matter in the sample is equal to the starch content expressed as % mass fraction.

5.2.2.2 Determination of moisture content

Determine the moisture content by the oven-drying method in accordance with ISO 1666.

5.2.3 Impurities

Not applicable (see 4.2).

6 Labelling - Transportation - Storage

6.1 Means of delivery

The product shall be delivered in suitable containers, e.g. bulk containers, sacks, drums or cans. Drums and sacks shall have a moisture barrier, e.g. an internal polyethylene liner.

In order that the purity of the product is not affected, the means of delivery shall not have been used previously for any different product or it shall have been specially cleaned and prepared before use.

6.2 Risk and safety labelling in accordance with the EU Directives

At the date of the publication of this standard, modified starches are not classified as dangerous substances according to EU Directive 67/548/EEC [3].

NOTE Annex I of the Directive 67/548/EEC on Classification, packaging and labelling of dangerous substances and its amendments and adaptations in the European Union contains a list of substances classified by the EU. Substances not in this Annex I should be classified on the basis of their intrinsic properties according to the criteria in the Directive by the person responsible for the marketing of the substance.

6.3 Transportation regulations and labelling

At the date of the present document, modified starches are not classified as hazardous for transport and do not therefore have a UN number[3)], hazard class, packaging group or require UN-certified containers.

6.4 Marking

Each container shall be marked with at least the following information:

a) the name "Modified starch", trade name and grade;

b) the net mass;

c) the name and address of supplier and/or manufacturer;

d) the statement "This product conforms to EN 1406".

6.5 Storage

6.5.1 Long term stability

Due to their slight hygroscopic nature, the products are best stored in a cool dry place, with low humidity and away from high temperatures. The products are usually stable for at least 12 months storage at ambient temperatures. Follow supplier's advice.

6.5.2 Storage incompatibilities

Store away from strong acids (e.g. sulphuric acid) and strong oxidizing agents (e.g. sodium hypochlorite). Avoid high humidity and temperature.

3) United Nations Number.

Annex A
(informative)

General information on modified starches

A.1 Origin

A.1.1 Raw materials

Modified starches can be manufactured from various raw materials such as potato, maize, wheat, barley, tapioca.

A.1.2 Manufacturing process

Non-ionic starch: an aqueous potato starch suspension containing 3 % mass fraction of $Na_2B_4O_7.10H_2O$ as calculated on starch is pregelatinized by heat. The viscous mass is transferred on to hot rotating drums in order to evaporate the water and to obtain the product as a dry millable film.

Cationic starch: unmodified potato starch is subjected to a reaction in an alkaline suspension with 2-hydroxy-3-chloropropyl-trimethyl ammonium chloride until a degree of substitution of approximately 0,035 - 0,7 is obtained.

Anionic starch: potato starch is carboxymethylated in alkaline solution by reaction with the sodium salt of monochloroacetic acid until a degree of substitution of approximately 0,113 is obtained. The reaction product is dried on rotating hot drums.

A.2 Use

A.2.1 Function

Starches are used in drinking water treatment to facilitate the removal of colloidal and fine suspended particles. They are effective when used in conjunction with metal salts in the removal of turbidity and colour.

A.2.2 Form in which it is used

Usually, the products are introduced into the treatment system as a dilute aqueous solution. It is recommended to first prepare fresh stock solution (approximately 5 % mass fraction), followed by appropriate dilution immediately before use to the required concentration.

A.2.3 Treatment dose

The treatment dose will vary depending on the quality of the raw water to be treated and can be subject to local regulations. Typically, a level of between 0,5 mg/l to 2 mg/l is used.

It is normal practice to allow a delay time between addition of metal salt coagulant and the product in order to minimize dosage requirement of the latter.

A.2.4 Means of application

The products are usually applied using a metering pump. Sufficient mixing action at the point of addition should occur to ensure adequate dispersion of the starch solution in the water being treated.

A.2.5 Secondary effects

The products have no secondary effects.

A.2.6 Removal of excess product

Not applicable.

A.3 Rules for safe handling and use

Good chemical handling practice should be followed at all times. Creation of dust should be avoided and the working environment should be kept clean and dry.

Spilled modified starches can result in a slipping hazard when mixed with water.

Prolonged contact can cause irritation of eyes.

Appropriate special risks should be entered on the safety data sheet to the effect that the product is slippery when wet:

a) in case of spillage, it should be swept up dry. The addition of water will render the floor very slippery and dangerous;

b) eye and hand protection is not normally warranted unless exposure is prolonged and in dusty conditions. Mild eye and skin irritation can result from extended contact;

c) protective clothing is not required on safety grounds, but overalls are recommended as cleaning can be problematic;

d) respiratory protection is not required providing ventilation is adequate and dust is controlled.

A.4 Emergency procedures

A.4.1 First aid

If modified starches are in contact with the skin, the contaminated area should be washed with copious amounts of soap and water.

If modified starches are in contact with the eyes, they should be rinsed with water for at least 15 min. If irritation persists, medical advice should be sought.

If modified starches are ingested, the mouth should be washed out with water but the affected person should not be allowed to swallow the wash water. Then water should be given to drink. An emetic should not be given. The affected person should be allowed to rest and medical advice should be sought immediately.

In addition to the above, any further advice on the supplier's safety data sheet should be followed.

A.4.2 Spillage

If spilllage is dry, it should be shovelled, vacuumed or swept up.

Modified starch flocculants are readily biodegradable and could therefore contribute to BOD and COD[4)]:

BOD_5 : approximately 500 mg of oxygen per gram of product;

COD : approximately 1 000 mg of oxygen per gram of product.

If a large spillage becomes wet, it should be contained with an inert material, such as sand or earth, to prevent it reaching the drains, and it should then be removed for disposal. Residues or small spillages can be flushed away with water. Spillages should not be disposed in watercourses.

A.4.3 Fire

Low fire and explosion risk. Products will not burn or support combustion easily. The following extinguishing media should be used: water, dry powder and foam.

4) The terms BOD and COD relate to Biological Oxygen Demand and Chemical Oxygen Demand respectively and indicate that if the material is flushed into a watercourse it could cause oxygen depletion.

Bibliography

[1] COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption

[2] Regulation EEC No. 4154/87. Official Journal of the European Communities No. L392/25. 31.12.87, page 19. Annex II. Determination of starches or dextrins or other modified starches content into goods of subheadings 3505 20 10 to 3505 20 90 of the combined nomenclature and of amylaceous substances content into goods of subheadings 3809 10 10 to 3809 10 40 of the combined nomenclature

[3] 67/548/EEC: Council Directive of 27th June 1967 on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances and its amendments and adaptations

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