SLOVENSKI STANDARD
SIST ISO 6293:1996

01-december-1996

Naftni proizvodi - Mazalna olja - Določanje števila umiljenja

Petroleum products -- Determination of saponification number

Produits pétroliers -- Détermination de l'indice de saponification

Ta slovenski standard je istoveten z: **ISO 6293:1983**

ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general

SIST ISO 6293:1996 **en**

International Standard ISO 6293

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Petroleum products — Determination of saponification number

Produits pétroliers — Détermination de l'indice de saponification

First edition — 1983-09-15

UDC 665.7 : 543.851.5 **Ref. No. ISO 6293-1983 (E)**

Descriptors : petroleum products, chemical analysis, determination, saponification number.

Price based on 5 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized 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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 6293 was developed by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, and was circulated to the member bodies in January 1982.

It has been approved by the member bodies of the following countries :

Australia	Iraq	South Africa, Rep. of
Austria	Ireland	Spain
Belgium	Israel	Sri Lanka
Brazil	Italy	Sweden
Bulgaria	Japan	Switzerland
Canada	Korea, Rep. of	Turkey
Egypt, Arab Rep. of	Netherlands	United Kingdom
France	Peru	USA
Germany, F.R.	Poland	USSR
Hungary	Romania	

The member body of the following country expressed disapproval of the document on technical grounds :

India

Printed in Switzerland

Petroleum products — Determination of saponification number

1 Scope and field of application

This International Standard specifies a method for the determination of the amount of constituents in petroleum products that will saponify under the conditions of the test. Since compounds of sulfur, phosphorus, the halogens, and certain other elements which are sometimes added to petroleum products also consume alkali and acids under test conditions, the results obtained include the effect of these extraneous materials in addition to the saponifiable material present. Results on products containing such materials, on used internal-combustion-engine crank-case oils and on used turbine oils shall be interpreted in this respect.

NOTE — The materials referred to above, which are not normally considered saponifiable matter, include inorganic or certain organic acids, most non-alkali soaps, etc. The presence of such materials increases the saponification number above that of fatty saponifiable materials for which the method is primarily intended. The odour of hydrogen sulfide near the end of the back-titration in the saponification test is an indication that certain types of reactive sulfur compounds are present in the sample. In the case of other reactive sulfur, chlorine, and phosphorus compounds and other interfering materials, no simple indication is given during the test. A gravimetric determination of the actual amount of fatty acids is probably the most reliable method for the estimation of such compounds.

2 Definition

saponification number : The number of milligrams of potassium hydroxide that is consumed by 1 g of oil under the conditions of the test as prescribed in this International Standard.

3 Principle

A test portion of known mass, dissolved in methylethylketone, is heated with a known amount of potassium hydroxide ethanolic solution. The excess alkali is titrated with standard volumetric hydrochloric acid solution and the saponification number calculated.

4 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical reagent grade, and only distilled water or water of equivalent purity.

4.1 Ethanol.

Purify 95 % (*V*/*V*) ethanol (see the note), or 95 % (*V*/*V*) ethanol to which has been added 10 % by volume of methanol, or absolute ethanol with silver oxide, in the following manner :

Dissolve 1,5 g of silver nitrate in about 3 ml of water, add to 1 litre of the ethanol in a glass-stoppered bottle, and mix thoroughly. Dissolve 3 g of potassium hydroxide in 10 to 15 ml of warm ethanol. After cooling, add slowly to the silver nitrate ethanolic solution, stirring slightly. Allow the precipitated silver oxide to settle, siphon off the clear solution, and distil on a steam-bath. Discard the first 5 % overhead, and also the final 5 %.

NOTE — It has been found that 99 % (*V*/*V*) 2-propanol (isopropyl alcohol) may be substituted for the purified ethanol with entirely satisfactory results. This substitution is not permissible however, in referee tests.

4.2 Potassium hydroxide, 0,5 mol/l ethanolic solution.

Prepare the solution by dissolving potassium hydroxide in the ethanol (4.1). Allow the solution to settle in a dark place. Dispense the potassium hydroxide (KOH) by siphoning or pressure from an inert gas so that any precipitate is not entrained. Allow the solution to stand for 24 h before using.

NOTE — Where saponification numbers below 1 are expected, better precision may be obtained by substituting 0,1 mol/l potassium hydroxide solution and 0,1 mol/l hydrochloric acid solution for the 0,5 mol/l reagents in 4.2, 4.3 and clause 8.

4.3 Hydrochloric acid, c (HCl) = 0,5 mol/l, standard volumetric solution.

Standardize frequently enough to detect concentration changes of 0,000 5 mol/l (see the note to 4.2).

4.4 Methylethylketone, technical grade.

Store the solvent in dark or brown bottles.

4.5 Petroleum spirit 60/80.

4.6 Phenolphthalein, neutralized indicator solution.

Dissolve 1 g of phenolphthalein in 100 ml of the ethanol (4.1). Neutralize to faint pink colour with 0,1 mol/l potassium hydroxide ethanolic solution.

5 Apparatus

5.1 Conical flask and condenser : A conical flask, 250 ml or 300 ml capacity, alkali-resistant (see the note), to which is attached an adequate straight or mushroom-type reflux condenser. The straight-type condenser shall be fitted to the flask with a ground-glass joint; the mushroom-type condenser shall fit loosely to permit venting of the flask. The glassware shall be chemically clean.

NOTE — It is recommended that flasks be cleaned with chromic acid cleaning solution or other suitable solvents and rinsed with distilled water. The used chromic acid cleaning solution shall be treated so as to render it harmless. Flasks that have become etched by long use should not be used. Hard borosilicate glass is suitable. New flasks sometimes give high values. Blank tests should be run concurrently on both new and old flasks.

5.2 Hot-plate : Suitable hot-plate heated by either electricity or steam.

5.3 Titration burette. A 50 ml burette with 0,1 ml subdivisions is suitable.

6 Blank test

6.1 Carry out one or more blank determinations concurrently with each set (see note 2) of samples as follows :

Measure from a burette or pipette (see note 3) into the conical flask (5.1) 25 ± 0,03 ml of the potassium hydroxide ethanolic solution (4.2) and 25 ± 1 ml of the methylethylketone (4.4). Connect the condenser to the flask, and heat for 30 min after refluxing begins (see note 4). Immediately add 50 ml of the petroleum spirit (4.5) (see notes 1 and 5) by cautiously pouring it down the condenser. (Disconnect the condenser if a mushroom-type is used.) Titrate the blank while hot, without reheating, with the hydrochloric acid solution (4.3), using 3 drops of the phenolphthalein indicator solution (4.6).

NOTES

1 Pouring 50 ml of petroleum spirit down the condenser at the end of the saponification not only rinses the condenser but also cools the reaction mixture.

2 Blank determinations should be run in duplicate on samples requiring the highest accuracy. The precision data are based on duplicate blank determinations. A single blank is sufficient for routine work.

3 If a volumetric pipette is used to measure the potassium hydroxide ethanolic solution, wait 30 s after delivery to allow for complete drainage.

4 Standard procedure requires that the mixture be refluxed for 30 min; however, it is known that some fats are readily saponified and complete saponification takes place within 10 min. On the other hand, some materials are saponifiable only with difficulty and are known to require more than 2 h in some cases. Neither the shortened period nor the longer period should be used except by mutual consent of the interested parties. The reflux time of the blank shall be the same as that of the sample in all cases.

5 In the case of insulating oils, the addition of petroleum spirit is not necessary.

6.2 When the indicator colour has disappeared, add, drop by drop, more indicator solution. If this addition of indicator restores the colour, continue the titration, making further drop by drop additions of indicator, if necessary, until the end-point is reached (see the note). The end-point is reached when the indicator colour has completely disappeared and does not immediately reappear upon further drop by drop addition of the indicator solution.

NOTE — Avoid emulsification of titration mixture, but assure phase contact, by swirling the flask vigorously as the end-point is approached.

7 Procedure

7.1 Test portion

The mass of the test portion shall be so chosen that the back-titration is from 40 to 80 % of the blank, except that the mass of the test portion shall not exceed 20 g.

NOTE — The following test portion sizes are suggested :

Saponification number	Test portion mass, g
181 to 400	1
111 to 180	2
71 to 110	3
31 to 70	5
16 to 30	10
0 to 15	20

7.2 Determination

Weigh the test portion to the nearest 0,01 g, by difference, from a small beaker into the conical flask (5.1). Add 25 ± 1 ml of the methylethylketone (4.4), followed by 25 ± 0,03 ml of the potassium hydroxide ethanolic solution (4.2) measured from a burette or pipette (see the note to 4.2 and note 3 to 6.1). Connect the condenser to the flask and heat for 30 min after refluxing begins (see note 4 to 6.1).

Immediately add 50 ml of the petroleum spirit (4.5) (see notes 1 and 5 to 6.1), by cautiously pouring it down the condenser. (Disconnect the condenser if a mushroom-type is used.) Titrate the solution while hot, without reheating, with the hydrochloric acid solution (4.3), using 3 drops of the phenolphthalein indicator solution (4.6).

When the indicator colour has disappeared, add, drop by drop, more indicator solution. If this addition of indicator restores the colour, continue the titration, making further drop by drop additions of indicator, if necessary, until the end-point is reached (see the note to 6.2). The end-point is reached when the indicator colour has completely disappeared and does not immediately reappear upon further drop by drop addition of the indicator solution. When testing waxes, it may be necessary to reheat the solution during titration to prevent solidification of the sample.

8 Expression of results

8.1 Method of calculation

8.1.1 Calculation of the saponification number

Calculate the saponification number by using the formula

$$\frac{56{,}1\ c(V_1 - V_2)}{m}$$

where

c is the concentration, in moles of HCl per litre, of the hydrochloric acid solution (4.3);

V_1 is the volume, in millilitres, of hydrochloric acid solution (4.3), used in the blank test (clause 6);

V_2 is the volume, in millilitres, of hydrochloric acid solution (4.3), used in the determination (7.2);

m is the mass, in grams, of the test portion (7.1).

For saponification numbers of less than 50, express the results to the nearest 0,5. For saponification numbers of 50 or more, express the results to the nearest whole number. For electrical insulating oils, express the results to the nearest 0,1.

8.1.2 Calculation of fatty oil content in compounded petroleum products

The percentage of fatty oil or fat in a compounded petroleum product can be calculated from the saponification number of such a product if the actual saponification number of the fatty oil or fat is known. If the actual number is unknown, but a sample of the added material is available, determine the saponification number of the additive and use in calculating the fatty oil or fat content.

If the actual saponification number is unknown and a sample of the added material is not available, the calculation for fatty oil content can be made with less accuracy, by using the average saponification number given in the table for the fatty oil or fat known to be present. In any case, the reported number shall be accompanied by a statement that the actual saponification number of the fatty oil was used in the calculation or that a stated, average number from the table was assumed to apply.

The foregoing procedure is not applicable to calculation of fat content of compounded petroleum products containing easily saponifiable or acidic constituents, of unknown properties other than the fatty oil or fat in question. However, if the saponification numbers of both the added fat in question and the base oil before blending with fat are known, the fatty oil or fat content, expressed as a percentage by mass, is given by the formula

$$100 \times \frac{C - B}{F - B}$$

where

C is the saponification number of the base oil containing added fat;

B is the saponification number of the base oil before blending with fat (see the note);

F is the saponification number of the fatty oil or fat added.

NOTE — If the blending material is an uncompounded refined base oil, the saponification number of the base oil (B) can be considered equal to zero in the above equation.

Table — Average saponification numbers of fatty oil or fat commonly used in compounded petroleum products

Fatty oil or fat	Saponification number	
	Average	Range
Castor	181	176 to 187
Coconut	256	251 to 261
Codliver	183	176 to 191
Cottonseed	194	187 to 197
Cottonseed, blown	218	210 to 225
Degras	*	85 to 150
Fish oil	*	100 to 200
Lard oil	195	190 to 198
Neatsfoot	197	193 to 204
Olive	193	189 to 197
Peanut	191	186 to 197
Rapeseed	175	170 to 179
Rapeseed, blown	205	195 to 216
Soybean	192	189 to 197
Sperm	128	120 to 140
Tallow, beef	197	194 to 200
Tallow, mutton	196	194 to 198

* The saponification numbers of degras and fish oil vary greatly according to their source and degree of refinement : therefore, it is not possible to give an average saponification number for these materials to be used for calculating the percent in base oils.

8.2 Precision

The precision of this method as obtained by statistical examination of interlaboratory test results, is as follows :

8.2.1 Repeatability

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the figure only in one case in twenty.

8.2.2 Reproducibility

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material would in the long run, in the normal and correct operation of the test method, exceed the values shown in the figure only in one case in twenty.

9 Identification of fat

In an unknown sample, particularly when a low saponification number leaves doubt as to whether fat is actually present, the fatty acid may be extracted (as the soap) and recovered for gravimetric determination.

10 Test report

The test report shall contain at least the following information :

a) the type and identification of the product tested;

b) a reference to this International Standard;

c) the result of the test (see 8.1);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.