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Paints and varnishes — Preparation of acid extracts from liquid paints

Peintures et vernis — Préparation des extraits acides des peintures liquides

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Foreword

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Paints and varnishes — Preparation of acid extracts from liquid paints

0 Introduction

This document is for use in conjunction with ISO 3856, *Paints and varnishes — Determination of "soluble" metal content.*

1 Scope and field of application

This International Standard specifies methods for the preparation of acid extracts required as the test solutions for the determination of the "soluble" metal contents of liquid paints and related products.

2 References

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1512, *Paints and varnishes — Sampling.*

ISO 1513, *Paints and varnishes — Examination and preparation of samples for testing.*

ISO 3856, *Paints and varnishes — Determination of "soluble" metal content.*

3 Definition

"soluble" metal content of paint : The metal content of the pigments and extenders soluble in a dilute acid of defined concentration plus the total metal content present in the liquid portion of the solvent-diluted paint.

4 Principle

Dilution of a sample of the liquid product to be tested, followed by centrifugal separation of the solid matter in the sample. Three methods, dependent on the medium of the paint being examined, are described for the separation of the solid matter.

Extraction with 0,07 mol/l hydrochloric acid solution of the separated solid matter (consisting of pigments and extenders).

Evaporation to dryness of the liquid portion of the product tested, obtained by centrifuging. Preparation of the residue for analysis by dry ashing and extraction of the ash with acid.

NOTE — 0,07 mol/l hydrochloric acid solution is chosen as an approximation to the acid strength in the stomach. It has been agreed that the mass ratio between the pigments and the hydrochloric acid solution shall be 1 : 15, except in the case of soluble lead where it shall be 1 : 1 000.

5 Sampling

Take a representative sample of the product to be tested by the method specified in ISO 1512.

6 Separation of the pigments and extenders from the paint sample

6.1 Preparation of the test sample

Examine and prepare the sample for testing as specified in ISO 1513. If any skin is present, remove it as far as possible. Thoroughly stir the sample and, if necessary, pass it through a sieve of nominal aperture 150 µm to remove any remaining skin and other extraneous matter.

6.2 Reagents

Select a solvent that effects the optimum separation of the pigments and extenders.

WARNING — In selecting the solvent to be used, possible toxic and other hazards and necessary precautions should be taken into consideration.

Examples of suitable solvents or solvent mixtures are as follows :

— for solvent-thinned paints, printing inks and similar products (method A) :

Toluene/ethanol (4 + 1) (for air-drying paints)
Xylene/1-butanol (9 + 1) (for stoving paints)
Toluene (for chlorinated rubber paints)
Butanone (for nitrocellulose paints)

— for emulsion paints based on aqueous polymer dispersions (method B) :

Acetone
Chloroform, freshly distilled
Tetrahydrofuran

— for plastisols and organosols based on polyvinyl chloride (PVC) and its copolymers and for paints based on non-aqueous polymer dispersions (method C) :

Tetrahydrofuran
Cyclohexanone
Cyclopentanone

6.3 Apparatus

Ordinary laboratory apparatus and glassware, and in particular

6.3.1 Suitable laboratory centrifuge, with tubes of inert material of capacity 50 or 100 ml. A centrifuge, capable of imparting a relative centrifugal acceleration of 100 km/s^2, is preferred.

6.3.2 Air-ventilated oven, capable of being maintained at 105 ± 2 °C.

6.4 Procedure

6.4.1 Method A (for solvent-thinned paints, printing inks and similar products)

Weigh, to the nearest 0,01 g, a number (see note 1) of centrifuge tubes (6.3.1). Add 10 to 20 g (see note 2) of the prepared sample to each tube, taking care to avoid contamination of the walls and lip of the tube. *Immediately* weigh the tubes and contents to the nearest 0,01 g. Approximately half fill the tubes with the selected solvent (6.2) and stir thoroughly using a glass rod. Wash the glass rods thoroughly with the solvent, adding all washings to the appropriate tube. Balance the opposing centrifuge tubes to within 0,1 g by adding further solvent, taking care to preserve an adequate working level. Centrifuge until there is a complete separation into a clear liquor and a pigment cake. Decant the supernatant liquor from all the tubes comprising a "set" (see note 1) into a stoppered glass container of approximate capacity 1 litre.

Add further solvent to each tube and mix thoroughly as specified above, taking care to completely disperse the pigment cake. Repeat the centrifuging and transfer of liquor. Repeat the addition of solvent, centrifuging and transfer of liquor for a third time, taking special care, as before, to disperse the pigment cake. As a final treatment for the pigment cake, use acetone in place of the selected solvent, to assist rapid drying. Add the acetone and mix, taking special care to disperse the whole pigment cake. Centrifuge and transfer the liquor as before to the stoppered glass container. Retain the container with the combined extracts for the procedure specified in clause 8.

After ensuring the evaporation of excess acetone, place the centrifuge tubes in the oven (6.3.2), maintained at 105 ± 2 °C, for a minimum period of 3 h. Remove, transfer to a desiccator, allow to cool to ambient temperature and weigh each tube and contents to the nearest 0,01 g. Return the tubes and contents to the oven for a minimum period of 1 h, allow to cool to ambient temperature in the desiccator and re-weigh. Repeat the heating, cooling and weighing operations until constant mass is reached; that is, until the results of two consecutive weighings do not differ by more than 0,01 g.

Calculate the pigment content of the paint as a percentage by mass of the paint sample (see note 3).

NOTES

1 Subsequent acid extractions should be carried out in duplicate and therefore sufficient paint and tubes should be taken so that at least 11 g of pigment is obtained. The number of tubes (usually four) required for each sample is referred to as a "set".

2 The mass of paint taken is dependent upon the capacity of the centrifuge tubes employed and on the expected pigment content of the paint.

3 If the dried pigment cake cannot be broken easily at the end of the extraction, this indicates that the binder has not been completely extracted.

6.4.2 Method B (for emulsion paints based on aqueous polymer dispersions)

Carry out the separation as specified in 6.4.1, but use acetone for the first and final treatment and the selected solvent for three intermediate treatments of the pigment cake.

6.4.3 Method C (for plastisols and organosols based on polyvinyl chloride (PVC) and its copolymers and for paints based on non-aqueous polymer dispersions)

Carry out the separation as specified in 6.4.1 but using a mass of sample such that it may be diluted with solvent in the ratio of 1 : 10. This ratio is necessary to obtain a practical sedimentation rate. Stir very thoroughly for sufficient time to convert the polymer from the dispersed to the dissolved state. Gentle heating may also be necessary.

6.5 Blank test solution

Prepare a mixture of the solvents in the proportions required for the separation. Retain for use as the blank in the determinations mentioned in clause 8.

7 Extraction of the separated pigments and extenders

NOTE — The mass of the solid material to be taken for the extraction may be reduced, for example because of a relatively high soluble metal content. In this case, the volume of the extraction liquid should be changed in such a manner that the original ratio of solid material to extraction liquid is maintained.

7.1 Preparation of the solid material

Take the dried pigment cake from all the tubes in one set obtained by the procedure specified in 6.4 and grind thoroughly in a mortar with a pestle until it passes through a 500 µm sieve (see note). Place the sieved pigment in a weighing bottle and transfer to the oven (6.3.2), maintained at 105 ± 2 °C, for 2 h. Store the bottle in a desiccator until required for further tests.

NOTE — It is essential that all the pigment passes through the sieve. Any pigment retained on the sieve, therefore, should be reground until it all passes through.

7.2 Extraction with hydrochloric acid solution

7.2.1 Method one

NOTE — The hydrochloric acid extract prepared according to 7.2.1 is used for the determination of "soluble" metals, other than lead, as described in ISO 3856 (see note to 7.2.2).

7.2.1.1 Reagents

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

7.2.1.1.1 Hydrochloric acid, 0,07 mol/l solution.

7.2.1.1.2 Hydrochloric acid solution, 1 + 1.

Dilute 1 part by volume of hydrochloric acid solution (ϱ approximately 1,18 g/ml) with 1 part by volume of water.

7.2.1.1.3 Ethanol, minimum 95 % (V/V).

7.2.1.2 Apparatus

Ordinary laboratory apparatus and glassware and, in particular

7.2.1.2.1 ***Suitable mechanical stirrer*** (see note 1).

7.2.1.2.2 pH meter and **electrodes.**

7.2.1.2.3 Membrane filter, pore diameter 0,15 µm, or other suitable filter capable of giving a clear solution.

7.2.1.2.4 Filtration apparatus, for the membrane filter (7.2.1.2.3).

7.2.1.3 Procedure

Carry out the extraction of the separated pigments and extenders in duplicate and protected from direct sunlight.

Weigh 5,0 ± 0,01 g of the prepared pigment sample (7.1) into a clean, dry 150 ml beaker. Wet the test portion with 2 ml of the ethanol (7.2.1.1.3), fit the stirrer (7.2.1.2.1) and add 75 ml of the hydrochloric acid solution (7.2.1.1.1) previously adjusted to 23 ± 2 °C. Immediately commence stirring the mixture (see note 1). Immerse a thermometer in the liquid, and adjust the temperature to 23 ± 2 °C. Insert the electrodes of the pH meter (7.2.1.2.2) and record the pH.

Continue stirring for 15 ± 1 min, ensuring that the temperature remains at 23 ± 2 °C during the whole period. If necessary, add the hydrochloric acid solution (7.2.1.1.2), drop by drop, during the extraction to maintain the pH at the original reading. At the end of this period of stirring, allow the mixture to stand for a further 15 ± 1 min at 23 ± 2 °C. Then filter through the membrane filter (7.2.1.2.3), using the filtration apparatus (7.2.1.2.4) and collecting the filtrate (which should be a clear solution) in a suitable glass container (see note 2). Immediately stopper the container (see note 3).

This acid extract shall serve for the determination of all metals other than lead (see 7.2.2) as required in ISO 3856. Appropriate aliquot portions should be taken for each determination.

NOTES

1 During the whole period of extraction, the speed of the stirrer should be adjusted so that the pigment is kept in continuous suspension while taking care to avoid splashing.

2 The whole of this operation should be completed in 10 min. Use only the filtrate obtained in this period.

3 Determine the acid-soluble metal content as soon as possible and at least within 24 h of the preparation of the hydrochloric acid extract. Longer storage of the extract can lead to false analytical results.

7.2.2 Method two

NOTE — The hydrochloric acid extract prepared according to 7.2.2 is used for the determination of acid-soluble lead as described in ISO 3856/1 (see note to 7.2.1).

Carry out the extraction as specified in 7.2.1 but take 0,5 ± 0,001 g of the prepared pigment sample (7.1) in a 1 000 ml beaker, add 2 ml of the ethanol (7.2.1.1.3) and 500 ml of the hydrochloric acid solution (7.2.1.1.1), stir for a period of 60 ± 1 min, and allow the mixture to stand for a further 60 ± 1 min.

7.3 Blank test solution

Take 2 ml of the ethanol (7.2.1.1.3) to which has been added either 75 ml or 500 ml, as appropriate, of the hydrochloric acid solution (7.2.1.1.1) and reserve for the blank determinations on the extracted pigments as specified in the appropriate parts of ISO 3856.

8 Extraction of the liquid portion of the paint

8.1 Reagents

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

8.1.1 Nitric acid, 1 + 1 solution.

Dilute 1 part by volume of concentrated nitric acid solution (ϱ approximately 1,42 g/ml) with 1 part by volume of water.

8.1.2 Hydrochloric acid, 0,07 mol/l solution. Use the identical solution prepared in 7.2.1.1.1.

8.2 Apparatus

8.2.1 Water bath.

8.2.2 Hot-plate.

8.2.3 Muffle furnace, capable of being maintained at 485 ± 15 °C.

8.2.4 One-mark volumetric flask, of capacity 100 ml, complying with the requirements of ISO 1042.

8.3 Procedure

Carry out the extraction of the liquid portion of the paint in duplicate.

Transfer the contents of the stoppered glass container, obtained according to 6.4, into a beaker of sufficient capacity (see note 1). Evaporate the main portion of the solvent, using the water bath (8.2.1) (see note 2). Transfer the remaining solution into a container suitable for ashing samples at 485 ± 15 °C. Evaporate to dryness (see note 3).

Place the container on the hot-plate(8.2.2) and slowly increase the temperature in order to remove all residual solvent. Gradually increase the temperature of the hot-plate until the material begins to char. Then transfer the container to the muffle furnace (8.2.3), maintained at 485 ± 15 °C, and ash (see note 4).

When the ashing is complete, remove the container from the muffle furnace and allow it to cool to ambient temperature. Break up the ash into fine particles with a glass rod and leave the rod in the container during the following filtration step (see note 5).

Add 10 ml of the nitric acid solution (8.1.1), taking care to avoid losses by splashing in case the ash reacts vigorously with the acid. Heat carefully on the hot-plate until 2 to 3 ml of solution remain. Add an additional 10 ml of the nitric acid solution and continue heating on the hot-plate until less than 5 ml of solution remain. Add 20 to 25 ml of water and filter the solution through medium-porosity filter paper into the 100 ml one-mark volumetric flask (8.2.4). If the filtrate is not clear, refilter through fine porosity filter paper. Wash the container and the filter paper several times with water. Dilute to the mark with the hydrochloric acid solution (8.1.2) and mix well.

This acid extract shall serve for the determination of all metals as required in ISO 3856. Appropriate aliquot portions should be taken for each determination.

Carry out the same procedure using the same quantities of all reagents on the blank test solution (6.5).

NOTES

1 If the paint sample contains cellulose nitrate, add 2 g of liquid paraffin to the liquid portion of the paint before removing the volatile solvents.

2 If desired, the bulk of the solvent may be removed by distillation.

3 If the paint sample contains chlorinated compounds, acidic products will be formed during ashing. Therefore, before ashing, mix with the residue obtained by evaporation to dryness of the combined extracts of the liquid portion of the paint sufficient anhydrous sodium carbonate to neutralize these products. As this procedure may require the addition of a relatively large amount of anhydrous sodium carbonate, it may be necessary to take an appropriate aliquot portion of the combined extracts.

4 Ashing at above 500 °C may result in the loss of some lead and cadmium by volatilization.

5 If the paint sample contains both antimony and lead, there is the likelihood of the formation of an insoluble compound which will be retained in the acid-insoluble residue; consequently low results will be obtained. To avoid these, ash the samples as directed, grind the ash to a fine powder, replace it in the same container and mix it with approximately six times its own mass of a mixture of equal parts of anhydrous sodium carbonate and sulphur. Cover the container and heat over a moderate flame until there is no odour of sulphur dioxide. This should take 1 to 2 h. Cool and digest with a small quantity of hot water until the melt is completely broken up. Filter, transfer the residue to the filter paper with a 1 % (*m*/*m*) sodium sulphide solution and wash the residue with the same solution. Dissolve the residue in the minimum quantity of boiling approximately 5 mol/l nitric acid solution, filter and wash with hot water into a 100 ml one-mark volumetric flask (8.2.4). Dilute to the mark with the hydrochloric acid solution (8.1.2) and mix well.