Overview of the test criteria examined in the approval tests of washing and cleaning agents

– Web-fed offset printing machines –

Dr Philipp Stolper

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Introduction

Since DRUPA 1990, low-emission washing and cleaning agents are available on the market. They are composed of very low-volatile hydrocarbon compounds, vegetable oils, esters of these oils or mixtures of these three material substances. At the launch of these products in the early nineties, technical problems regarding the compatibility of the cleaning agent with some printing machine parts like rubber rollers, machine paintwork, tubes or seals, etc. arose. To be able to lessen the emissions caused by volatile washing and cleaning agents in offset printing and to limit the risk of machine damage at the same time, printing machine manufacturers along with Fogra, the BG ETEM (German institution for statutory accident insurance and prevention in the printing and paper processing industry), the Bundesverband Druck und Medien (The German Printing and Media Industries Federation) and the trade union “IG Medien” (since 2001 part of ver.di) initiated the formation of a voluntary undertaking: The ‘industry initiative for the reduction of solvent emissions in offset printing’.

The participants in this initiative have agreed upon the following recommendations for the use of washing and cleaning agents, based on the current state of safety engineering and environmental protection:

- Flash point over 60 °C
- Benzene content < 0,1 %
- Toluene and xylene content < 1 %
- Aromatic content (from C9) < 1 %

The following substances may not be used:

- Halogenated hydrocarbons
- Terpenes
- n-Hexane
- Secondary amines or amides
- Nonylphenol
- N-Methylpyrrolidone (NMP)
- 2-Butoxyethanol
- Ingredients whose use is linked with unacceptable health risks based on the current state of knowledge regarding occupational health and toxicology. You will also find information about this under the following link: http://emissionsarme-produkte.bgetem.de/

Blanket and roller washing and cleaning agents that are employed on sheet-fed offset printing machines must be tested for their compatibility with the most important materials from the machine. These compatibility tests mainly include 3 areas:

1. Physical and chemical properties of the product such as iodine number, non-volatile portions, viscosity, stability of the formulation, emulsification characteristics with water, miscibility with organic solvents and the water content.
2. Compatibility with elastomeric materials from the machine. These include ink, wash-up and dampening rollers, ‘metal back blankets’, as well as elastomeric machine parts like seals and rubber pipes.
3. Compatibility with metallic materials in the machine. These include corrosion tests on metallic materials (steel, nickel, brass) and durability tests on machine paintwork, printing plates and metal parts.

The following document supplies a detailed description of difficult testing criteria. Washing and cleaning agents that do not obtain approval, often fail to fulfil one or more of the difficult testing criteria. Other test criteria from the aforementioned overview do not usually present a problem.

Universally valid characteristic for every washing and cleaning agent formulation

Iodine number

The Iodine number (IZ), as the measured value for saturation of a compound, gives information about the stability of the product (-> shelf life) and about the tendency towards auto-ignition. It is determined according to DIN/ISO 3961. Iodine numbers > 20 are allowed for certain product formulations used in heatset and coldset printing. However, if your product has a iodine number > 20, you will need to have a confirmation from BG ETEM that your product meets their criteria as they were presented at their meeting on 20th May 2015 in Mainz. Please contact Dr Nadine Metz for further information (e-mail: Metz.Nadine@bgetem.de or telephone: +49 (0)611 / 131-8172).
Difficult testing criteria

1. Physical and chemical properties of the cleaning agent

1.1 Stability of the cleaning agent formulation

Problems can arise in storage or in practical use in the washing system below certain temperatures or at room temperature/operating temperature due to changes in the cleaning agents (e.g. flocculation of components or variations in concentration in the container). Solid components can cause blockages in automatic washing systems and thus make the use of the cleaning agent impossible.

Test method: ‘Stability at room temperature’

To test the stability of the formulation, the cleaning agent is centrifuged twice for 20 min at 4000 revolutions/min. It is examined whether drops of slimy matter have collected on the base of the test tube or whether other visible changes such as precipitation have occurred.

Centrifuge data:
Hettich Centrifuge Universal 16 A
Swinging bucket rotor with centrifuge tubes (filling capacity: 40 ml – 50 ml)
Distance centre-centrifuge tube base during rotation: ca 132 mm

Test method: ‘Stability at lower temperatures’

To test whether flocculation occurs in cleaning agents through cooling, 40 ml of cleaning agent is kept for 4 h at a temperature of –5 °C (Cryostat). The cleaning agent is immersed in a cryostat bath (IPA-water solution) in a sealed test tube and the test tube is filled almost completely with cleaning agent. After 4 h it is examined visually whether changes, especially flocculation or phase separations, have occurred. It is recorded whether these changes are reversible at 10 °C (cleaning agent is stored at 10 °C for about 18 h) or at room temperature (20 °C).

1.2 Emulsification characteristics with water and miscibility with organic solvents

The mixing behaviour with water is of particular importance in case of washing processes on printing machines. Emulsions can be formed, which can differ sharply in their viscosity characteristics from the undiluted product. Highly viscous or even solidifying aggregates can cause major problems in automatic washing systems. Similarly, possible changes in the fluid characteristics of the product can take place. Appearance of solids and changes in colour and viscosity are of particular importance. In case of products with such effects, use in washing systems cannot be recommended. The duration for which the emulsion (cleaning agent and water) remains stable is also recorded.

Test method: ‘Stability at lower temperatures’

To determine sticky, non-volatile residues in the cleaning agent, which – particularly in the past – have repeatedly given rise to problems in printing machines (e.g. clogging of nozzles and pipes), are determined in this test.

Test method:

To test whether flocculation occurs in cleaning agents through cooling, 40 ml of cleaning agent is kept for 4 h at a temperature of –5 °C (Cryostat). The cleaning agent is immersed in a cryostat bath (IPA-water solution) in a sealed test tube and the test tube is filled almost completely with cleaning agent. After 4 h it is examined visually whether changes, especially flocculation or phase separations, have occurred. It is recorded whether these changes are reversible at 10 °C (cleaning agent is stored at 10 °C for about 18 h) or at room temperature (20 °C).

1.3 Determination of non-volatile residues and impurities

Sticky and/or non-volatile residues in the cleaning agent, which – particularly in the past – have repeatedly given rise to problems in printing machines (e.g. clogging of nozzles and pipes), are determined in this test.

Test method:

To determine sticky, non-volatile residues in the cleaning agent, the volatile components are eliminated in the drying cabinet for at least 24 h by means of evaporation at 80 °C and atmospheric pressure. For this, a drying cabinet UFF 500 from Memmert is used. The air flap on the air slide valve is open to the maximum (fresh air regulation) and the ventilator speed (air circulation regulation) is set to 100 %.

3-5 drops (ca. 100 mg – 150 mg) of the cleaning agent are placed on the lower plate of a previously weighed glass disc (Heidbrink flat weighing glasses) and covered with the top plate. The two plates are rubbed together to make the sample spread into a thin film. The mass of the applied cleaning agent is determined. Caution is needed that cleaning agent does not drip from the glass disc, as this can lead to deviations in meas-
The glass disc is placed in the drying cabinet at 80 °C (the top plate is lifted on to the hook of the cradle). The testing time is 24 h. Weighing is done after cooling down to room temperature. The glass discs should be thoroughly cleaned between the different samples.

Limits: The amount of cleaning agent that is left on the glass disc after attenuation weight constancy is described as residue. The amount of solvent residues for VOC-containing washing and cleaning agents should not exceed 5 %. VOC-free products are allowed to show solvent residue levels of up to 20 %.

The criteria for VOC-free products are method 24 of the EPA (US Environmental Protection Agency) and California’s regulations 4 which define a VOC-free product as not exceeding a limit of 100 g/l. A description of the test procedure for a method 24 measurement is available on Fogra’s website.

### 2. Durability of non-metallic materials

#### 2.1 Durability of “metal back blankets”

The tests are based on DIN 53521 [Test of rubber and elastomers: Determination of the performance in the presence of fluids, vapours and gases] and a practice-oriented model system. The swelling characteristics of the material samples are to be determined. The tester uses the recommended test devices and test specimens. The swelling characteristics of the cleaning agent is characterised through mass change.

In case of metallic blankets, defined test flaps from the manufacturers Reeves, Day International, Conti Tech and MacDermid are used. The machine manufacturer manroland provides the appropriate metal blankets for pre-tests.

The swelling tests are performed with undiluted cleaning agent as duplicate measurement. A 100 ml DURAN®-bottle based on ISO 4796 with a red cap (PBT/PTFE), which can be autoclaved up to 180°C, is used for the test.

**Test method:**

The aim of the procedure is to determine with $m_0$: mass before exposure and $m_i$: mass $m_i$ to $m_9$ after exposure/airing

$$A^* = 0,5625$$

(Correction factor $A_{inner}/A_{total}$)

Further, all changes in colour and form and other unexpected defect patterns are to be listed under ‘Others’.

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Airing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration</td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td>24 h</td>
</tr>
<tr>
<td>3 h</td>
<td>48 h</td>
</tr>
<tr>
<td>24 h</td>
<td>7 d</td>
</tr>
<tr>
<td>Determin. of $m_1$ - $m_9$</td>
<td></td>
</tr>
<tr>
<td>$m_1$</td>
<td>$m_7$</td>
</tr>
<tr>
<td>$m_2$</td>
<td>$m_8$</td>
</tr>
<tr>
<td>$m_3$</td>
<td>$m_9$</td>
</tr>
</tbody>
</table>

The geometry of the test specimens

- CuZn37 (MS 63): 2.0321, DIN 17660).
- as brass shavings (copper-zinc alloy CuZn37 (MS 63): 2.0321, DIN 17660).
- nickel test pieces, as well as mixed with water. As an increase in corrosiveness is expected in the second case, the following tests are performed:

  Recording of the anodic current-density potential curve and determination of the passivation current density and, if necessary, the break-through potential. Determination of mass loss at free corrosion during total immersion as a function of time with calculation of the area-related mass-loss rate. The test specimens are steel (100 Cr6 G3K2) and nickel test pieces, as well as brass shavings (copper-zinc alloy CuZn37 (MS 63): 2.0321, DIN 17660).

The washing and cleaning agents used in web-offset printing are used undiluted as well as mixed with water. As an increase in corrosiveness is expected in the second case, the following tests are performed:

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- Corrosion test of metallic materials
(steel and nickel) is concurrent to the measurements used for the testing of dampening solution additives.

**Test method:** The test fluid is defined as follows:

*Water-soluble cleaning agent*

Water-soluble cleaning agents that form a monophase mixture after mixing with the test water in the ratio of 1:1 are described as stable emulsions. They are used to perform electrochemical tests (E).

**2-Phase systems**

For these cleaning agents the aqueous phase that has separated after mixing with water and a 24-hour waiting period is used to perform the electrochemical tests (E). The organic phase is used to perform the total immersion tests (T).

The total immersion tests and the electrochemical tests with steel and nickel are performed along the lines of the dampening solution test. The total immersion test with brass shavings is performed as follows:

5 g brass shavings are mixed in a specimen jar with 80 ml a) undiluted cleaning agent or d) the organic phase from a 2-phase mixture in the case of instable emulsions. The staining of the shavings and the clouding of the cleaning agent after 7 days at room temperature is assessed.

**The valid limits are defined as follows.**

**Results of the electrochemical test:**

The course of the current-density potential curve in the anodic region after exceeding the free corrosion potential is of importance. A steep rise indicates a rapidly rising material conversion. Here it is of interest whether the material is re-passivated at current densities below 10 μA/cm² or whether the material conversion is correspondingly inhibited, so that this value is only exceeded by about 800 mVH –potentials that are no more relevant in practice.

All cleaning agent-water combinations that produce a curve progression, which does not exceed a maximum current density of 10 μA/cm² for nickel in the potential range up to +800 mVH, and a maximum current density of 50 μA/cm² for steel in a potential range of the free corrosion potential up to +1200 mVH, are suitable.

**Results of the total immersion test with steel and nickel:**

Staining and possibly the mass loss before and after exposure are assessed.

<table>
<thead>
<tr>
<th></th>
<th>Steel</th>
<th>Nickel</th>
<th>Brass</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Non-water-soluble cleaning agents</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) stable 1:1 emulsion or micro-emulsion</td>
<td>Total immersion test if &lt;100 μS/cm; electrochemistry if &gt;100 μS/cm</td>
<td>Total immersion test if &lt;100 μS/cm; electrochemistry if &gt;100 μS/cm</td>
<td>Total immersion test</td>
</tr>
<tr>
<td>c) unstable emulsion – aqueous phase</td>
<td>Total immersion test if &lt;100 μS/cm; electrochemistry if &gt;100 μS/cm</td>
<td>Total immersion test if &lt;100 μS/cm; electrochemistry if &gt;100 μS/cm</td>
<td>Total immersion test</td>
</tr>
<tr>
<td>d) unstable emulsion – organic phase</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The area-related mass-loss rate in mg/cm² after 7 days is determined.

Here the following limit values are valid:

Steel: ≤ 15 mg/(cm²·7d)

Nickel: ≤ 3 mg/(cm²·7d)

**Results of the total immersion test with brass:**

- Light bluish colour, but transparent solution
- Mild concentration gradients (streaks)

**Criteria for ‘not OK’:**

- Visible changes of the brass shavings (e.g. staining)
- Clouding
- Precipitations/flocculation/sediment
- Phase separations

**3.2 Durability of machine paintwork and printing plates with respect to washing and cleaning agents**

It is recommended to test the durability of machine paintwork and printing plates beforehand. Commercially available conventional as well as ctp printing plates should be tested to assess the durability of printing plates. The criterion for durability is that the paint surface or the plate layer should not be attacked by the cleaning agent.

**Test method ‘Machine paintwork’:**

Undiluted cleaning agent is used as the test fluid, if no deviating concentration is specified by the manufacturer for the application. For the test of multiple-use washing and cleaning agents fresh and filtrate solution are used for the test. A 100 ml DURAN® bottle with a red cap according to ISO 4796, which can be autoclaved up to 180°C, (PBT/PTFE) is used for the test. The test specimen consists of a sheet of 1 mm thickness as carrier for a standard coating. The test specimens are punched out as discs and have a diameter of 40 mm. For the test with a glass bottle, a test specimen (machine paint) with a diameter of 40 mm (diameter of the area of interaction is 30 mm) is required. The test specimen is placed in the lid so that the painted surface is facing the medium. According to DIN 53 521 the volume of the test liquid to be used should be at least 15 times in relation to test specimen. 50 ml of the test fluid is filled into the glass bottle. The Duran glass bottle is screwed securely and placed upside down and
stored in the oven at a temperature of 40 °C ± 1 °C for 7 days.

The evaluation takes place on the basis of an optical assessment in 4 categories:
Category 0: no visible changes
Category 1: light, visible changes
Category 2: strong, visible changes
Category 3: machine paintwork destroyed

Assessment in categories 2 and 3 leads to a termination of the test. Further, all changes in colour and form and other unexpected defect patterns are to be listed under ‘Others’.

Test method ‘Printing plate durability’:
Fogra carries out a collective plate test for all machine manufacturers and types. The plates to be tested are selected by the plate manufacturers, updated when required and delivered. The selection was/will be complemented through products chosen by the machine manufacturers.

The plate test is generally carried out under yellow light. When testing UV washing and cleaning agents, the printing plates are first baked for 5 min at 230 °C – if they are designed for such treatment. Test strips of standard negative and positive printing plates (conventional as well as ctp) are exposed briefly with UV light (ca. 5 s) – this simulates the influence of daylight in the print-room – and subsequently immersed in the cleaning agent for 10 min. The cleaning agent is wiped off 3 times with a cleaning cloth applying a standard force of 60 N (adjustable with the Fogra ‘Fiwi’). The magnitude of the staining of the ink-accepting layers on the cleaning cloth is a qualitative measure for the durability of the image on the printing plate.

The assessment is visual, based on the following criteria:
Category 0:
No staining or only very light staining on the cleaning cloth and no alterations or only very light visually noticeable alterations of the plate image.

Category 1:
Staining on the cleaning cloth and/or smudging of the plate image.

Category 2:
Strong staining on the cleaning cloth and/or strong smudging of the plate image.

Category 3:
Destruction of the plate image.