

Health and Safety Executive OC 687/7

Field Operations Division

To

Factory Inspectors

FCG Specialist Inspectors (Process Safety and

Occupational Hygiene)

THE HAZARDS ASSOCIATED WITH THE SILVERING OF MIRRORS, VACUUM FLASKS, ETC

This OC revises and updates the advice given in FIC 687/1 on the main hazards to be safeguarded against during various types of silvering and associated processes.

Background

1 The production of silvered surfaces is commonly achieved by the chemical reduction of a silver salt to the metallic state. This process is mainly used to produce vacuum flasks and mirrors, but it is also employed in the silvering of glass, plastics and other materials for artistic and decorative effects. There are other substances which can be used for special types of mirror (eg gold and lead sulphide), but these will not be discussed here. This circular will describe the process for the silvering of glass, but the silvering of other materials is very similar.

2 In the past silvering was generally considered to be an art carried on secretly by craftsmen and even today there are silverers who will not reveal the details of their process, even to their own management. The backstreet silverer is now, however, becoming more of a rarity in the face of competition from the large automatic systems which are being introduced. Even so, there will always be a need for the small silvering business which will undertake the one-off jobs and those that cannot be carried out economically on the conveyor belt.

Materials

3 The chemicals required for the deposition of silver are silver nitrate, ammonia, sodium (or potassium) hydroxide, a reducing agent and deionized water. Apart from the latter, these are purchased either as basic materials for formulating *in situ*, or as ready-prepared solutions which only require dilution and application. The main suppliers of silver nitrate are:

(1) Engelhard Industries Ltd (2) Johnson Matthey Chemicals Ltd

Cinderford 74 Hatton Garden

Gloucestershire London EC1

4 There is, however, a tendency now to purchase pre-formulated solutions. At the moment the suppliers of such solutions are: London Laboratories Ltd, Woodbridge, Connecticut, USA, and Johnson Matthey Chemicals Ltd, London. The reducing agent is normally a sugar such as sucrose or glucose but occasionally, hydrazine sulphate and formaldehyde are used. New types of reducer are being developed by the suppliers of pre-formulated solutions.

5 Water purification is usually carried out on site and where an ion-exchange method is used, inspectors will find solutions of hydrochloric (or sulphuric) acid and sodium hydroxide nearby. These are used in the regeneration of the ion-exchange resin.

6 Stannous chloride (or sulphate) solution or solid will be found in all silvering works, and in most there will be copper sulphate, sulphuric acid and hydroxylamine (London Laboratories Solution CV-1-C). These are used before and after the deposition of the silver mirror, as described in paras 7 and 13.

Basic silvering process

7 The glass is thoroughly cleaned and then treated with a solution of stannous chloride or sulphate. This process is often called tinning or sensitising, and its purpose is to promote the deposition of the silver on the surface. There should be little hazard associated with this procedure, short of ingestion of the tinning solution.

8 There are many variations of the silvering process, but they all involve certain basic procedures. Ammonia is added to silver nitrate solution to form a silver/ammine complex. The main effect of the ammonia is to prevent the precipitation of insoluble silver oxide. To this complex solution is added an alkali solution (usually sodium hydroxide) and a reducer solution. In the presence of the alkali, the reducer converts the silver/ammine complex into metallic silver, which is deposited as a mirror.

9 The whole art of mirror manufacture is to bring together these various chemicals so that the silver is deposited quickly when applied to the glass, but not before. If silvering is carried out by hand, the ingredients are either mixed just before application, or allowed to meet on the glass, so that reduction cannot take place too early. However, application by spraying is used almost exclusively nowadays, and the method falls readily into 2 categories; manual spraying and automatic spraying. These will be described more fully in paras 11 and 12.

10 Many silverers are very secretive about the actual compositions of their formulae. In every case, however, the solution applied to the glass contains about ½% W/V (½ gram silver nitrate in a 100 ml solution) silver, with the ammonia, alkali and reducer present in similar amounts. Stock solutions are made up in a more concentrated form for eventual dilution to the silvering concentration.

11 Manual spraying is normally carried out in a ventilated booth. The solutions are nearly always made up by the silverer, usually to a commercial formula. Inspectors may come across such terms as the Steinhardt Process and the Schweig Process, which are variations on the standard silvering method. Spraying is mostly carried out using a 2-part system, the reducer and silver/ammonia/alkali solutions being made up in separate containers. They are delivered to the gun by separate lines and mix in the atomised spray. It is important to ensure that the concentration of the silver solution never exceeds the maximum limit recommended (see para 15).

12 The automatic spray method is carried out on a conveyor belt. Solutions are either made up *in*

situ, or are purchased in a prepared form. There are 2 distinct types of automatic spray method, one using a 2-part and the other a 3-part system. The 2-part system is essentially the same as that described in para 11, but in the 3-part system, the silver/ammonia, alkali and reducer are all supplied separately to the gun, and mix in the atomised spray. This is the safest method as it removes the need to mix the silver/ammonia and the alkali (see paras 14-19) until just before the reduction takes place.

13 When the silver has been laid on the glass, it is usually protected by a layer of copper. This is achieved by spraying (or pouring) onto the silver coating a solution of copper sulphate in sulphuric acid to which a solution of hydroxylamine has been added. There should not normally be a dust explosion hazard under the conditions prevalent in a silvering shop. After drying, a final protective coat of paint is added.

HAZARDS

Explosion

14 The main hazard associated with the silvering process is the formation of the well-known explosive "fulminating silver". This is a black precipitate which is generally accepted to be a mixture of silver nitride (Ag_3N), silver imide (Ag_2NH) and, possibly, silver amide (AgNH_2). This mixture is formed by the reaction of silver on ammonia in the presence of an alkali. There is evidence to show that a high alkalinity (pH greater than 13) is required before the reaction can proceed. Several explosions have occurred in the silvering industry but, in most cases, the silver concentration was 10% W/V or greater.

15 For many years, HSE has recommended that the maximum concentration of a stock silver solution should be 6% W/V. This is 10-12 times more concentrated than the silvering concentration, and there is reason to believe that such solutions should not present an explosion hazard. It is often argued that solutions of silver and ammonia alone can be more concentrated than this as the absence of alkali prevents the formation of fulminating silver. There has, however, been a number of accidents where alkali was not consciously added to concentrated silver/ammonia solutions, and it is reasonable to assume that such solutions became contaminated in some way. Laboratory tests indicate that the amount of alkali required to raise the pH of a silver/ammonia solution to 13 or more is of the order of 4%. With the exception of the London solution (see para 17), no silver nitrate solution should be more concentrated than 6% W/V. Contamination with alkali may occur if the wrong solutions are inadvertently mixed, and it is important therefore that containers of solutions and reagents are clearly labelled to identify their contents.

16 Time is another hazard. Dilute solutions can concentrate by evaporation of water, and explosions have occurred when silver solutions have been left to stand. Silvering solutions should, therefore, be used immediately to avoid any possibility of the formation of unstable compounds. Excess solutions should not be kept.

17 Solutions supplied by London Laboratories Ltd of USA are now made up to a special formulation which is protected by patents. In this system, a reducing agent is present in the ammoniacal silver solution supplied. Alternatively, London Laboratories supply the reducing agent in a "silverless solution" that the manufacturer adds to his own ammoniacal silver nitrate solution. The reducing agent will not reduce the silver until an alkali, which is supplied separately, has been added. Since the formation of fulminating silver also depends on the presence of alkali, the hazard is removed as the reduction to silver is faster than the formation of explosive side-products. Although silver solutions made with London Laboratories formulations range from 12.5-25% W/W, there is no reason to object to their storage and use.

18 There are 2 other silver compounds which are often confused with fulminating silver. Silver azide

(AgN₃) is a white, unstable compound which can be formed by the addition of sodium azide to a silver solution. It is difficult to visualise circumstances in which a silverer would need sodium azide, and so the hazard is a very remote one. Silver fulminate (AgONC) is said to be formed by the reaction of a silver compound with ethyl alcohol. The product is white and is reported to explode by touch when dry. This, again, is an unlikely hazard in the mirror industry, but the presence of alcohol (eg meths) near a silvering process should be discouraged.

19 There have been reports of explosive reactions during the making up of the alkali solution. The dissolution of sodium hydroxide in water is highly exothermic and the addition of water to solid alkali can result in the violent emission of hot solution and steam. The alkali should always be added carefully, with stirring, to an excess of water.

Health hazards

20 In those premises where the solutions are made up from constituents, there are the usual problems associated with handling chemicals. Acids and alkalis are corrosive and so protection for the skin and, especially, the eyes is required. Special care will be needed in factories where etching is carried out to give a decorative effect, as this process normally involves the use of hydrofluoric acid, a very corrosive material.

21 Ammonia is given off during the silvering process and there should be a good standard of general ventilation to prevent fumes accumulating in the workshop. The gas has a OES of 25 ppm but can be detected by smell at 5 ppm and is readily noticeable at 20 ppm. At 100 ppm it becomes a nasal irritant, and at about 400 ppm it becomes destructive to moist skin and mucous membranes. Under normal conditions, the solutions will be fairly dilute and should not lead to high concentrations of gas. Where solutions are made up by hand, however, very concentrated ammonia solutions may be found and these should always be handled in exhaust ventilated enclosures. The spray booth may have sufficient ventilation for this purpose, otherwise a fume cupboard or similar enclosure will be required. Proper carriers should be used to transport glass bottles within the works.

Flammable vapours

22 Some sections of the industry may use screen printing after silvering to produce picture mirrors or decorated glass for pinball and other games machines. After conventional silvering, silver is removed from the areas to be printed with an acidic solution of ferric chloride. There are both health and fire hazards, guidance on which is given in the PIAC booklets, *Safety in the use of inks, varnishes and lacquers cured by ultraviolet light or electron beam techniques*, and *Fire safety in the printing industry*, (file 711).

23 After the application of the silver and copper, a protective coat of paint is applied either manually or, in the case of an automatic line, by a curtain or roller coater. The applicator should be covered but it is not usually necessary to ventilate it. General exhaust ventilation may suffice for this part of the process. The painted mirrors are normally dried in a tunnel oven and attention should be paid to the provision of explosion relief and adequate ventilation.

24 The area of explosion relief should be not less than half the top of the drying oven. This may be effected by allowing sections of the top to lift whilst ensuring that they do not become dangerous missiles in the event of an explosion. To prevent dangerous concentrations of flammable vapours accumulating within the drying ovens, it is recommended that fresh air should be induced into the oven at a rate of 60 m³ per litre of solvent to be evaporated. This should dilute the vapours to 25% of the lower explosive limit. It is also recommended that air-flow switches be fitted in exhaust ducts, and so wired that the heating system and the conveyor cannot be energised unless the recommended

air-flow rate has been achieved. Further guidance on solvent evaporating ovens is contained in the HSE Guidance Note HS(G)16, *Evaporating and other ovens*, (file 291) (currently under review).

Residues

25 Because of the high value of silver, all residual solutions are treated for the recovery of their metal content. There are a variety of recovery methods but the most popular is to collect effluent in large settling tanks where it is left for 6-12 months. There should not be much danger in this process as the solutions will be no richer than the silvering concentration. There have been no reports of accidents during the digging out of the residues. Some firms, however, throw excess stock solutions into the settling tanks, and there is always a remote possibility of the formation of unstable substances. The refiners of the residues recommend the acidification of these solutions with dilute hydrochloric acid. This will remove any possibility of the formation of fulminating silver. It has the added attraction of increasing the silver recovery rate as any silver still dissolved will precipitate out as silver chloride. If it is thought that acidic conditions may lead to corrosion of the settling tanks, reinforced fibre glass tanks could be recommended.

26 Some silverers dry the residues on hot surfaces prior to despatch to the reclaimer. The presence of ammonia could lead to the formation of fulminating silver on heating. Therefore residues to be dried should be washed until they are free of ammonia.

Cancellation of instruction

27 FIC 687/1 - cancel and destroy.

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ASI headings

Chemicals - use of: explosions: glass: mirrors: silvering: vacuum flasks - manufacture.