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Methods of cleaning glass by vapour degreasing and ultrasonically agitated solvents

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The production of clean glass surfaces for vacuum evaporation purposes has been studied using a number of different chemical cleaning techniques. The principal cleaning methods investigated were vapour degreasing, using a range of solvents, and high- and low-frequency ultrasonic agitation of an *iso*propyl alcohol bath. The cleanliness of glass surfaces after treatment was assessed from their coefficient of friction, wetting properties and adherence to vacuum deposited coatings. In terms of these properties vapour degreasing in pure *iso*propyl alcohol produced the cleanest surface. However, low-frequency ultrasonic agitation was the most effective method of removing gross surface contaminants. The cleaning of intricately shaped components is briefly discussed and it is shown that the gas pressure above the cleaning medium must be initially reduced to allow the solvent to enter cavities and thus provide maximum irradiation of the surface. Ultrasonic cleaning was found to be most effective when operated at low frequency (25 kc/s) with an undegassed fluid under atmospheric pressure.

A number of techniques have been advocated for preparing highly clean glass before depositing thin films on its surface by vacuum evaporation. Undoubtedly one of the most efficient methods of cleaning a glass surface is to immerse it in a glow discharge and much of the work on this subject has been reviewed by Holland.[1] Recent work done in this laboratory has shown that the most effective cleaning agency in the glow discharge is the bombardment of the glass surface by positive ions and high energy neutral molecules, whereas electron irradiation of the surface may give rise to the formation of contaminant films.[2] Glow discharge cleaning cannot remove gross contaminants from a surface, although uniform coatings of many molecular layers in thickness may be removed. Experiments were at first undertaken to determine the best chemical method of removing thick contaminant layers from glass surfaces before submitting them to glow discharge cleaning. However, in the course of these experiments it was found that under certain conditions clean glass surfaces could be prepared which were equal to those with a glow discharge.

Chemical methods of cleaning glass involving detergents, hydrocarbon solvents and acids are well described in the literature (see, for example, Strong[3]). Acid cleaning can be injurious to the surfaces of certain types of glasses and for this reason was not considered in these investigations. One of the simplest methods of cleaning glass is to wash the surface with a detergent and water followed by cleaning with cotton-wool steeped in a solvent such as *iso*propyl alcohol. Another and more effective process for removing molecular contamination from glass surfaces is by vapour degreasing in an alcohol vapour, a method which has become fairly well established in the lens-coating industry. Ultrasonic agitation of cleaning fluids has also been used successfully for removing gross contamination, e.g. rouge and pitch from the surfaces of optical components.[4] Each of the foregoing processes has been investigated to determine the standard of surface cleanliness it is capable of producing, and to find whether it can produce glass surfaces of comparative cleanliness to that obtained with ionic bombardment.

EXPERIMENTAL

The test glasses used in the experiments to be described were, with few exceptions, 2 mm thick uncoated lantern slides made of green soda-lime. The manner of employing the different cleaning processes are described below after a discussion of the techniques used for determining surface cleanliness.

(*a*) *Assessment of cleanliness*

There are various simple tests which can be used to find whether a glass surface is free from molecular contamination after treatment and these can be summarized as follows.

(i) *Breath figures and wetting.* The breath condensate formed on a clean glass surface exists as a uniform water layer because of the affinity of the clean glass for water. Such a breath figure has been termed "black" to differentiate it from the "grey" breath figure which is formed on contaminated glass and is due to the formation of minute water globules in the condensate (see, for example, Rayleigh,[5] Baker[6] and Fraser[7]). Similarly, a water droplet placed on a clean surface immediately flows outwards over the surface, whereas on a contaminated glass it forms a droplet with a measurable contact angle. Both the wettability and the type of breath figure were studied for the glass surfaces cleaned by the processes described in these experiments.

(ii) *Coefficient of friction.* A glass surface free from monomolecular contaminating layers has a high coefficient of friction (μ) to metals and glass as shown by Langmuir.[8] Values of the static coefficient of friction of about 0·8 have been obtained in this laboratory for glass on glass after the surface has been cleaned with Teepol and alcohol and bombarded in a glow discharge.[2] In the tests made in these experiments the static coefficient of friction (μ) was measured

in air, directly after cleaning, using a glass rider cut from $\frac{1}{4}$ in. thick plate, with a contact area of 2 × 5 cm. The rider was maintained in a clean state at all times by continuously degreasing it in *iso*propyl alcohol vapour. Values for the kinetic coefficient of friction were obtained by vibrating the specimen surface at 50 c/s during measurement.

(iii) *Thin film adhesion.* Evaporated metal films generally adhere more strongly to glass when the substrate has been thoroughly cleaned, so that the resistance shown by a metal film to stripping is a simple measure of the effectiveness of the pre-cleaning. This is particularly true for evaporated aluminium which was used in these experiments. The adhesion of the aluminium was tested by stripping the metal film with Sellotape pressed on to its surface.

(*b*) *Detergent washing and solvent cleaning method*

The test surface was first washed in a detergent (Teepol) and distilled water to remove heavy gross contaminants and then thoroughly rinsed and dried using a soft cloth. The glass was then polished with a soft absorbent cloth soaked in *iso*propyl alcohol. When the solvent had completely dried off the surface, a final polish was given with a Selvyt cloth. The results for the standard of cleanliness achieved are shown in Table 1, showing that the coefficient of friction (μ) of a surface cleaned with a detergent only is lower than one cleaned finally with a solvent. However, the values of μ obtained with both treatments rose to the same value after ion bombardment for 10 min at 3000 V and 500 mA in an 18 in. diameter bell jar. This shows that the solvent cleaning stage can be omitted provided the Teepol washed surface is glow-discharge cleaned.

Table 1. *Values for the static and kinetic coefficient of friction for glass surfaces cleaned by solvent and detergent cleaning methods*

Method of cleaning	*Coefficient of friction* Static	Kinetic
Vapour degreased in *iso*propyl alcohol	0·5–0·64	0·4–0·62
Vapour degreased in trichlorethylene	0·39	0·31
Vapour degreased in carbon tetrachloride	0·35	0·28
Teepol washed and polished	0·07	0·04
Teepol washed and h.t. discharge cleaned	0·8	0·6
Teepol washed, cleaned with alcohol and chalk, wiped with cotton-wool	0·33	0·27
Teepol washed, cleaned with alcohol, wiped with cotton-wool and h.t. discharge cleaned	0·8	—
Vapour degreased in *iso*propyl alcohol and h.t. discharge cleaned	0·8	0·6
Teepol washed, cleaned with alcohol and chalk, wiped with cotton-wool and flamed with gas flame	0·41	—

The value given for each cleaning method is a mean value resulting from several tests with that particular technique.

(*c*) *Vapour degreasing*

The vapour degreasing process was carried out in a large glass beaker, which was heated on an electric hot plate. The glass surfaces being cleaned were first washed in Teepol to remove heavy contamination. Three solvents were tested in sequence, namely carbon tetrachloride, trichlorethylene and *iso*propyl alcohol. The glass slides were suspended in the vapour for periods ranging from 15 s to 15 min. Maximum cleaning was achieved after an immersion period, which generally corresponded to the time taken for the condensing vapour to heat the glass to the temperature of the saturated vapour so that condensation ceased. Obviously the greater the thermal capacity of the specimen body the longer would be the time for which condensing vapour washes the exposed surface. If, however, the thermal capacity of the specimen is low, then it is possible for its surface to reach the temperature of the saturated vapour before the vapour has effected maximum cleaning. In the event of this it is necessary to immerse the specimen in the vapour a number of times. However, these tests indicated that effective cleaning can be obtained within a small time interval of about two minutes.

The highest value for the coefficient of friction obtained by vapour degreasing was 0·64 using *iso*propyl alcohol as the cleaning agent (see Table 1). Of the chemical cleaning methods investigated this technique gave a coefficient of friction nearest to that obtained by ion bombardment. Good results for the adhesion of evaporated aluminium were also obtained, as demonstrated in Fig. 1.

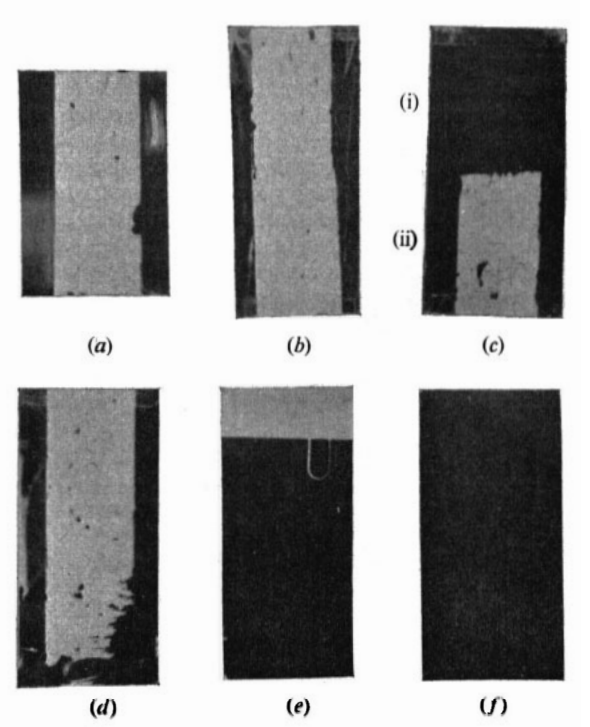

Fig. 1. Results of Sellotape stripping tests carried out on aluminium coatings deposited upon surfaces pre-cleaned by the following methods:

(*a*) Teepol washed and polished with soft cloth, no discharge cleaning; (*b*) vapour degreased then immersed in Teepol and water solution and allowed to dry, no discharge cleaning; (*c*) (i) vapour degreased, (ii) immersed in *iso*propyl alcohol and allowed to dry.

No discharge cleaning; (*d*) ultrasonically cleaned using high frequency agitation in *iso*propyl alcohol, no discharge cleaning; (*e*) vapour degreased in *iso*propyl alcohol, no discharge cleaning; (*f*) vapour degreased in *iso*propyl alcohol and discharge cleaned.

The results obtained with *iso*propyl were still maintained when the cleaning was carried out in a large stainless steel container suitable for cleaning 2 ft square glass plates with a steam-heated alcohol boiler. However, it was found necessary, especially when cleaning a relatively large specimen with high thermal capacity, to withdraw it slowly from the

vapour, allowing time for any condensate tears which may be still on the surface to evaporate off. When tears were left to dry off on the surface in air their marks or figures appeared after vacuum coating and in these regions the adhesion was always very poor.

Both carbon tetrachloride and trichorethylene produced low values for μ and poor film adhesion. The inferior results obtained with these two solvents are partly attributed to the loose whitish residue which appeared on the glass surface after vapour degreasing. If the deposit had been due to volatile impurities in the solvents then it should have re-evaporated from the glass when it became hot. The persistence of the deposit suggested that it was a chloride produced by reaction between the solvents and constituents in the glass surface.

(d) Ultrasonic cleaning methods

The use of both low- and high-frequency ultrasonic agitation of cleaning fluids for industrial purposes is discussed by Atherton[9] who considers the cleaning effect of cavitation in the agitated fluid. It is shown that the phenomenon, which is present at the lower frequencies (20 to 100 kc/s) will greatly assist the removal of gross particles from contaminated bodies. High cavitation energies can damage the surface of the article being cleaned and therefore the energy output of a low-frequency system must be carefully controlled. High energies can be used with high-frequency systems having frequencies of the order of 1 Mc/s, because the cleaning action is more gentle and free from cavitational bombardment of the irradiated surface. Noltingle and Neppiras[10] have investigated the problems of cavitation and its dependence on vibration frequency, internal pressure and the presence of nuclei of suitable size for its production.

There are certain conditions which arise by reducing the pressure above the liquid in agitation, which may or may not

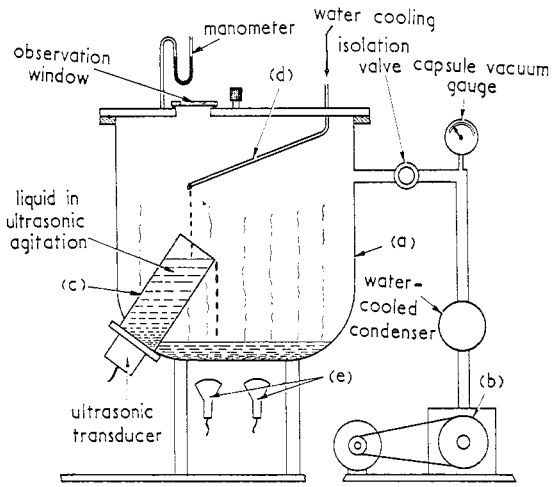

Fig. 2. Apparatus used for ultrasonic cleaning

be advantageous when cleaning surfaces.* The two main factors introduced are as follows:

(1) dissolved gases which provide suitable nuclei for cavitation centres are removed, and therefore cavitation effects may be reduced.[11]
(2) air trapped in deep holes in the surface of intricately shaped components may be removed, thereby permitting the solvent to cover completely the surface to be cleaned.

The influence of these two effects and the standard of cleaning obtainable with ultrasonics were observed using an apparatus constructed as shown in Fig. 2. With this system, cleaning could be conducted either at atmospheric or reduced pressures.

Ultrasonic cleaning apparatus

The vacuum chamber *a* was evacuated using a rotary pump *b* having a pumping speed of 450 l./min; the pump was fitted with air ballasting. The vessel *c* isolated the fluid in ultrasonic agitation from the solvent contained in the chamber. A condensing system *d* was fitted in the chamber lid to produce a continuous exchange of fluid by distillation from the chamber into the vessel *c* so that fluid was kept clean. For distillation the liquid was heated externally by two infra-red heaters *e*.

The ultrasonic power was provided by either a high-or low-frequency ultrasonic generator. The high-frequency unit operated at 1 Mc/s and had a 300 W output. A thin slice of barium titanate crystal was used as the transducer with an effective area of 4 × 8 cm. The low-frequency unit operated at 25 kc/s at an output of 250 W using a magneto-strictor for the transducer, the vibrating plate was approximately 10 cm in diameter. The transducer mountings were suitably constructed to fit into the vacuum system as shown in Figs. 3 and 4. In view of the effectiveness of *iso*propyl

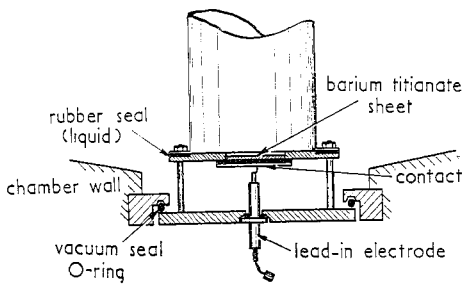

Fig. 3. High-frequency transducer (barium titanate crystal)

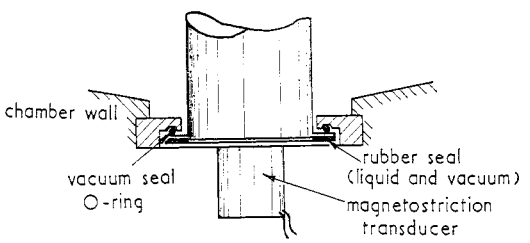

Fig. 4. Low-frequency transducer

alcohol when used in vapour degreasing it was decided to restrict the ultrasonic tests to this fluid.

Ultrasonic experiments

The cleaning liquid was degassed under a controlled pressure of between 30–50 mm of mercury, i.e. in the region

* An ultrasonic cleaning system, in which the fluid is agitated under reduced gas pressure, is manufactured by the Technochemie Co. of Switzerland.

of the saturated vapour pressure of the solvent at room temperature. Further degassing occurred when the liquid was ultrasonically agitated. In fact, when using the low-frequency agitation the boiling of the liquid was violent unless the generator was operated at reduced power. However, in the high-frequency case conditions were stable enough for carrying out cleaning tests using maximum power input. The slides were cleaned for periods of from fifteen seconds up to several minutes. After each operation the solvent was allowed to dry by evaporation to ensure that the final state of the surface was due to the ultrasonic cleaning, and not interfered with by wiping or polishing. Tables 2, 3 and Fig. 1 indicate the standard of cleanliness obtained using ultrasonics under these conditions.

Table 2. *Static and kinetic coefficient of friction results for ultrasonically cleaned glass surfaces*

	High-frequency cleaning		*Low-frequency cleaning*		
Time (s)	*Static*	*Kinetic*	*Static*	*Kinetic*	*Comments*
15–20	0·39	0·28	—	—	High-frequency generator run at full power, 300 W
30–45	0·39	0·27	—	—	
60	—	—	0·3	0·2	
120	0·4	0·27	0·28	0·2	Low-frequency generator run at half power, 125 W
5 min	0·37	0·25	0·3	0·2	

The values given are mean values resulting from many tests.

The highest value achieved for the static coefficient of friction was 0·4. It was not easy to explain why there should be a difference in the cleaning results between the vapour degreasing and ultrasonic cleaning methods. In the first technique the test surfaces were immersed in a very pure alcohol vapour and in the second the surfaces were immersed in the very pure distilled alcohol liquid itself. Both samples in their respective cleaning medium should then be exposed to equivalent surface contamination, if any. A number of theories were discussed but no conclusions were arrived at. Radiant heating of the glass surface to accelerate drying after removal from the fluid did not alter the results. However, h.t. discharge cleaning in a vacuum cleaned off the residual contamination responsible for the low friction values as shown by adhesion tests (see Fig. 1).

Table 3. *Wetting observations for different cleaning methods*

Method of cleaning	*Observation*
Ultrasonically cleaned in *iso*propyl alcohol using high frequency at reduced pressure	Only slight indication of wetting
Ultrasonically cleaned in *iso*propyl alcohol using low frequency at reduced pressure	Only very slight indication of wetting
Vapour degreasing in *iso*propyl alcohol	Surface wets
Discharge cleaned in correctly designed systems	Surface wets
Teepol washed and polished	No wetting
Vapour degreased in either carbon tetrachloride or trichlorethylene	Partial wetting

A series of tests were carried out on unwashed slides with both low- and high-frequency ultrasonic cleaning which showed that heavy contaminants, such as greasy finger prints, could be removed from a glass surface when exposed to ultrasonic agitation providing the fluid was at atmospheric

Table 4. *Removal of heavy dirt deposits*

The glass slides were heavily finger-printed with grease and dust. Two greases were used: Apiezon vacuum grease and ordinary lubricating oil.

Method of cleaning	*Cleaning ability*	*Comments*
Immersed in *iso*propyl alcohol for 2 min	No cleaning	Oil contamination only
Immersed in trichlorethylene for 2 min	No cleaning	Oil contamination only
Ultrasonically cleaned at atmosphere for 2 min in *iso*propyl alcohol. Using high-frequency transducer	Removed grease and dirt, but not the finger print impression	Oil contamination only
Ultrasonically cleaned at reduced pressure for 2 min in *iso*propyl alcohol using high-frequency transducer	Removed grease and dirt, but not the finger print impression	Oil contamination only
Ultrasonically cleaned at atmosphere for 2 min in *iso*propyl alcohol using low-frequency transducer	Removed both grease and dirt and completely removed finger print impression	Will clean oil prints off in ½ min
Ultrasonically cleaned at reduced pressure for 2 min in *iso*propyl alcohol using low-frequency transducer	Removed both grease and dirt and completely removed finger print impression	Will clean oil prints off in ½ min
Vapour degreased in *iso*propyl alcohol	Removed grease and dirt, but not finger print impression	—

Table 5. *Cleaning of enclosures using ultrasonic methods*

Closed ended tubes and capillaries	Ultrasonic cleaning at atmosphere using low-frequency transducer in *iso*propyl alcohol. Trapped gases not removed	Colloidal carbon (Dag)	No cleaning
Closed ended capillary	Ultrasonic cleaning at reduced pressure using low-frequency transducer in *iso*propyl alcohol	Colloidal carbon (Dag)	Partial cleaning after 4 min
Closed ended capillary	Low-frequency transducer in *iso*propyl alcohol. System pumped out to remove trapped air from capillary. Air admitted to system. Ultrasonic cleaning carried out at atmosphere in undegassed medium	Colloidal carbon (Dag)	Complete removal after approximately 4 min

The exact times required for removing a particular contaminant could not be obtained because of the variation in quantity of contamination from specimen to specimen in the many repeated runs.

pressure and agitated at a low frequency (see Table 4). These results show how cavitation is essential for removing gross contaminants. The effectiveness of the ultrasonic cleaning of enclosures was determined using glass capillary tubes 1·5 mm diameter × 2 cm long with closed ends. The inside surfaces were contaminated with colloidal carbon (Dag) or grease. The tests demonstrated that it is necessary to reduce the gas pressure above the cleaning medium to remove the trapped air from the holes and interstices to obtain maximum irradiation of all surfaces, but in order to achieve the most effective cleaning the liquid should again be in an undegassed state as shown in Table 5. This again shows the need for cavitation when removing gross contaminants. The standard of the cleaning obtained after the removal of the major contaminants could not be assessed, but it was assumed to be of similar order to that achieved on the flat glass surfaces.

CONCLUSIONS

The investigations show that vapour degreasing in *iso*-propyl alcohol produces a higher standard of surface cleanliness than can be achieved with ultrasonic cleaning. The failure to obtain comparable results with ultrasonic agitation was not easy to explain as stated above. It was found that vapour degreasing in *iso*propyl alcohol could produce clean surfaces which were almost comparable to those obtained by discharge cleaning. However, this method was not found to be efficient in the removal of gross contamination and must therefore be used in combination with a detergent washing process. The vapour degreasing and ultrasonic methods are both suitable as pre-cleaning techniques for preparing glass supports for thin film deposition, provided discharge cleaning is used, especially in the ultrasonic case, in the final treatment.

It was shown that, to obtain uniform cleaning of intricately shaped surfaces when using ultrasonics, a vacuum system must be used in order that the pressure above the cleaning medium can be initially reduced to release trapped gases from enclosures. However, it was found that the fluid should be in an undegassed state and agitated at low frequency to obtain the most effective cleaning, demonstrating the importance of cavitation for the removal of gross contaminants.

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Technique for determining the orientation of single crystals of bismuth

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Except in particular cases, neither X-rays nor light figures alone suffice to determine completely and unambiguously the orientation of a bismuth crystal rod. The technique described consists of a combination of the two. The light figure pattern is used to locate the (111) plane approximately in order to aline the rod relative to the X-ray beam before the back-reflexion Laue photograph is taken, and to assist in the interpretation of the stereographic projection. The modifications made to a Unicam single-crystal X-ray goniometer to enable the technique to be applied to rods of 6 mm diameter and 25 cm length are described.

The orientation of a metal single-crystal rod, that is the angles which the principal crystallographic axes make with the rod axis, may be determined either from back-reflexion Laue photographs of the crystal using X-rays or from the optical reflexion patterns, so called "light figures," obtained from the etched surface of the crystal. In the case of bismuth neither method may prove conclusive. However, by a careful combination of the two methods it has been found possible to determine completely and unambiguously the orientations of single-crystal rods of bismuth, about 6 mm in diameter and of lengths ranging up to 25 cm. The details of the technique and procedure are described in the next section. The technique is applicable both to crystals of high quality and to crystals exhibiting a gross macromosaic structure of the type described by Teghtsoonian and Chalmers.[1]

Bismuth is trigonal, and its primitive cell consists of a simple rhombohedron with an axial angle of 57° 14′. It is more useful, however, to characterize the structure by a face-centred rhombohedron formed from the primitive cell (see Salkovitz[2] and Vickers[3]), and in addition, this face-centred rhombohedron may be regarded as a face-centred cube which has been slightly deformed by extension along a diagonal until the axial angle becomes 87° 34′. The diagonal corresponds to the trigonal axis. Vickers[3] has published tables of the angles between the crystallographic directions and between the planes of the bismuth lattice, and he has discussed how back-reflexion Laue photographs of bismuth crystals can be interpreted. However, because of the near cubic symmetry of the bismuth lattice, it is not possible to obtain an unambiguous interpretation of the photographs of