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THE USE OF HYDROGEN FLUORIDE IN THE DEVELOPMENT OF LATENT FINGERPRINTS FOUND ON GLASS SURFACES

HERBERT L. MACDONELL

The use of hydrofluoric acid for the development of latent fingerprints on glass surfaces has been suggested by several investigators (1). In each instance, however, the use of hydrofluoric acid, an aqueous solution of the gas hydrogen fluoride, is suggested rather than the use of hydrogen fluoride itself. This investigation was conducted using hydrofluoric acid vapor, a mixture of hydrogen fluoride and water vapor, rather than liquid hydrofluoric acid. The choice of the acid vapor is based upon the well established fact that the destruction of fingerprint detail is greatly increased with an increase in the density of the developing medium. For example, a gas or vapor technique such as iodine or osmium tetroxide fuming should be one of the first methods considered for the development of latent fingerprints (1) (2) (3) (4) (5). If these methods can not effectively be employed in a given situation, then liquid or solution development procedures should be considered (1) (2) (4) (6). Finally, the use of solid powders when dusting, rolling, or spraying should be considered as a last resort (1) (2) (4) (7). Even though they receive the last consideration, solid methods will still find the most frequent application as vapor and liquid techniques tend to be highly selective for paper, wood, and other rough or porous surfaces. The use of liquids which may be cured to semi-solid elastomers has recently been introduced for lifting fingerprints (8). It might be well to consider the use of these new materials before resorting to solid procedures; however, once such a method has been attempted it is doubtful that subsequent procedures will yield usable results. The medium upon which a latent fingerprint is deposited will, of course, be a determining factor in the selection of a development method. If such a fingerprint were left on a piece of window glass of a normal composition (9), it has been found that the use of hydrofluoric acid vapor will yield detail superior to that which is obtainable by other development procedures. In addition, the development process renders the fingerprint absolutely permanent by all reasonable standards of physical and chemical durability. Fingerprints thus developed actually become a part of the glass surface by being etched into the glass and will withstand any degree of weathering that could have been tolerated by the original piece of glass before treatment. A piece of glass processed in this manner may be filed with confidence as it will never become smudged and will definitely not deteriorate with age.

DEVELOPMENT MECHANISMS

The reactions between hydrofluoric acid and silicates are well understood (10). Etching or dissolving glass in hydrofluoric acid may be expressed by the chemical equation:

$$6HF + Na_2SiO_2 \rightarrow SiF_4 + 2NaF + 3H_2O$$

wherein sodium silicate represents a $Na_2SiO_3$-SiO$_2$ glass network in the reaction. According to Farncomb (11) the additional reaction:

$$3SiF_4 + 3H_2O \rightarrow H_2SiO_3 + 2H_2SiF_6$$

also takes place as the decomposition occurs in the water solution. The presence of CaO, MgO, K$_2$O, BaO, B$_2$O$_3$, Al$_2$O$_3$ and other constituents found in glass compositions (9) is not taken into consideration in the above reaction as the destruction of the silica network is fundamental to the solution of these other metal oxides. Furthermore, while the investigation did establish the adaptability of the method to many glasses of unusual or uncommon composition, it is unlikely that glass objects other than windows, mirrors, bottles, or drinking glass-
ware will often be submitted as evidence bearing latent fingerprints.

There is some confusion as to the physical mechanisms involved in the selective etching of glass surfaces by hydrofluoric acid vapor on glass upon which latent fingerprints have been deposited. At room temperature a piece of glass which has been coated with a film of grease or wax will not be "wetted" by water or aqueous solutions. This repulsion offered by the waxy substances in a latent fingerprint to the etching action of hydrofluoric acid is the basis for the use of this acid in the conventional development of fingerprints on glass (1). Theoretically, when a piece of glass is submerged in hydrofluoric acid etching will occur in every area not protected by a film of grease or wax such as would be deposited by the friction ridges of a finger. Therefore, if a piece of glass containing a latent fingerprint were so treated the fingerprint would protect specific areas and result in a liquid development method. In theory it would seem that this method would be highly successful and therefore desirable. In practice one achieves little success in obtaining reproducible results. In no instance has the author ever felt that the results obtained following this procedure were superior to those which could have been obtained had the fingerprints been developed by careful dusting. An explanation for the shortcomings of the liquid hydrofluoric acid method may be stated briefly in the following paradox: If the concentration of the acid is too high then the submersion time of the glass must be very critically controlled. Dilution of the acid will allow a longer submersion time; however, this increased soaking time permits acid penetration of the grease or wax barrier to such a degree that considerable etching takes place even in the friction ridge areas.

In view of this dilemma only a small effort was made with liquid hydrofluoric acid etching of glass as a practical means of fingerprint development. The possible use of hydrofluoric acid vapor for the same purpose presented itself as a possible solution to the problems described above for two reasons. First, the concentration of the reagent would be considerably lower in the vapor phase and thus longer exposures could be tolerated without excessive etching and ultimate destruction to the entire glass surface. This longer exposure time would allow considerably greater reproducibility. Second, the vapor would not produce a soaking effect on the grease or wax deposits and little etching, if any at all, would occur in the friction ridge areas. It was assumed, therefore, that hydrofluoric acid vapor development would yield superior results to the liquid analog. In addition, it was believed that the basic character of the reaction would remain unchanged so long as the same reagent was used. While the first assumption was correct, the second was entirely incorrect producing exactly the opposite from the predicted result.

**Apparatus**

Initial experimentation was conducted in a rather small polyethylene container having no provision for vapor circulation. Fingerprints developed in this apparatus had a somewhat spotted surface with respect to etching. It is possible that the vapor was composed of several gradient layers of different density and composition. Overlapping of these layers could have been the cause of poor reproducibility. Some fingerprints developed using the vapor over hydrofluoric acid were excellent; however, others were either not etched sufficiently, were unevenly etched, or were so badly etched that detail was destroyed beyond all usefulness. In every instance, without regard to the degree, etching always occurred within the area of the fingerprint impression itself. This phenomenon was entirely contrary to the predicted results described above. Apparently, hydrofluoric acid vapor is selectively absorbed by the fingerprint deposit to such a degree that considerable etching takes place in this area while little or no action occurs on the rest of the glass. Hydrofluoric acid vapor consists of both hydrogen fluoride and water vapor. It is possible that water vapor is initially absorbed by the fingerprint and that hydrogen fluoride is subsequently absorbed into this water thereby forming hydrofluoric acid in the fingerprint pattern. The acid would thus be confined to the fingerprint impression and would produce etching only in this area.

In an effort to achieve more reproducible results a larger container was obtained, formed from polyethylene as shown in figure 1. A small paddle was fashioned from sheet polyethylene and polyethylene tubing fitted over a glass rod for rigidity. The large polyethylene container used in this study was manufactured by Tupperware of Orlando, Florida. The small polyethylene container was cut from the bottom of an empty hydrofluoric acid bottle. Likewise, the polyethylene used to fabricate the fan was cut from the side of an empty hydrofluoric acid bottle and worked into shape with a hot glass rod. The polyethylene tubing and hydrofluoric acid were purchased from Arthur H. Thomas of Philadelphia, Pennsylvania and Baker & Adamson (General Chemical Division of Allied Chemical) of New York City, respectively. A Sargent Synchronous Rotator, 600 RPM constant speed motor (E. H. Sargent and Co., Chicago) was used. 

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A glass rod was rotated by a small motor and provided an even stirring action for the hydrofluoric acid vapors. This motor was placed below the polyethylene container as shown in the figure for two reasons, first; both hydrogen fluoride and water vapor are lighter or less dense than air, therefore, the corrosive acid vapor would diffuse upward away from the container; second, by placing the stirring assembly below the container the hole required for the stirrer would be on the bottom of the large polyethylene container and no difficulty would be encountered in removing or replacing the cover (not shown) between samples. This location of the stirrer hole necessitates the use of a smaller dish for holding the hydrofluoric acid and may be seen in the lower right corner of the large container in Figure 1.

**PROCEDURE**

Prior to placement within the large polyethylene container for development, samples should be generously smeared with Vaseline on the opposite side from that which bears latent fingerprints. This operation is performed to prevent etching of both sides of the glass at once as normally fingerprints will appear on only one side of a piece of glass. Thus prepared, the sample is placed in the apparatus taking care to see that the greased side faces downward and rests on the short polyethylene supports. These supports may be cut from tubing and are shown supporting the glass sample in Figure 1. Noticeable vibration from the fan motor may cause the polyethylene supports to rub grease from the bottom side of the glass and thereby result in undesirable etching in these areas. A small piece of polyethylene sheet pressed against the bottom greased surface will eliminate this problem. In the event that both sides of a sample bear latent fingerprints no grease should be used on either side. The side upon which the better appearing fingerprints are deposited should be on top during development. In addition, the glass must be carefully placed so that the supports do not destroy detail in the fingerprints on the lower side.

After the glass sample has been prepared as described above and has been placed into the apparatus for development, 48% hydrofluoric acid is carefully poured into the smaller container. A large cover is placed over the apparatus in a loose fashion, and the fan motor is turned on. Two to two and one-half hours are normally required for achieving the optimum in etching glass of normal composition (9). The exact time must be determined experimentally using a piece of glass of the
same composition as that upon which the evidence fingerprints are deposited. A fresh fingerprint placed upon a separate piece of glass may be conveniently prepared for this purpose. Following development the glass may be washed in hot water to remove the Vaseline. If the cover is placed on the apparatus too tightly poor results will be obtained as the etching will be non-uniform.

RESULTS

Fingerprints processed in this manner give every appearance of a latent fingerprint, however, they are very permanent and may be washed or rubbed without damage. Contrast is somewhat low between the etched or frosted portion of the glass and its background as shown in Figure 2. Rubbing this etched surface with a relatively soft pencil will greatly increase the contrast by the deposit of graphite into the rough etched patterns. This subsequent development procedure results in a positive black fingerprint of remarkable detail on a clear glass background. In the event appreciable etching has occurred between the friction ridges it may become necessary to brush the graphite from this area using a piece of cloth in much the same manner as one uses a brush for removing excess powder when dusting a fingerprint. This condition results when glass is exposed for too long a period and should be avoided.

After a glass sample has been properly processed as described above it is placed into a photographic enlarger with the fingerprint side of the glass down corresponding to the emulsion side of a negative. The projected image of the fingerprint is brought to focus within a 4 x 5” area and an exposure is made directly onto Cronar Ortho A film. The film is processed in the normal photographic manner resulting in a negative of even greater contrast than the original positive. The final enlargements produced from the 4 x 5” negatives may be seen in Figure 3.

DISCUSSION

One of the many possible ramifications offered by this development procedure is the subsequent projection of colored fingerprints of both suspect and evidence for comparison study. If a suspect were caused to place a fingerprint on a piece of glass, it could be processed with a color different from the one used in processing the evidence glass. By the superimposed projection of both colored fingerprints onto the same screen the points of comparison would be indicated by the color resulting from the mixing of the two separate colors. Points of dissimilarity would be indicated by the two individual colors of each original piece of glass.

When fingerprints occur on both sides of the same piece of glass it is still possible to complete the above development procedure, however, only
FINGERPRINT DEVELOPED WITH HYDROGEN FLUORIDE

one side of the glass may contain graphite at a
time when projecting a fingerprint image. After
one side has been used to obtain a 4 x 5" negative
the graphite is removed from this fingerprint, and
the second side is processed in a like manner.

Although no effort was made to study the
effects of temperature and humidity on this
development method it should be pointed out that
time apparently has little or no effect as to the
final results. The impressions illustrated in figure
2 were developed over ten days after being made.
An investigation to establish these relationships
and the correlation of data to the work of Bluhm
and Lougheed is anticipated (12).

As to sensitivity it can only be stated that it is
possible to obtain better results with this procedure
than with dusting. It is not possible to develop the
same fingerprints by both methods so that this
statement must be based upon treatment of
samples prepared at the same time, but developed
differently. Sensitivity, however, is the ability to
develop a very poor fingerprint, that is, the limit
of resolution. Acceptable results were obtained
from both methods so that this does not ade-
quately evaluate sensitivity.

In one respect vapor development which does
not cause brush marks or streaks due to external
movement abrading the latent fingerprint means
that this method has superiority. Further vapor
will not fill in and thus destroy pore detail.

The glass to be developed by this method should
be taken to the laboratory. While this presents
some problems with large unbroken pieces the
nature of the crime determines the thoroughness
of the investigation. In some instances the cost of a
piece of plate glass would be very little when
compared to the crime. The method would find
its most wide-spread application to breaks wherein
the perpetrator gains his entrance by breaking a
small glass window and deposits his fingerprints
while removing the pieces.

As for a very important final advantage to this
method it should be pointed out that photographically speaking the method has much to
offer. Conventional dusting requires subsequent
photographing of the developed fingerprint and
final projection for an enlargement. In the method
described no camera is required. The glass itself
being used as a positive eliminates focusing errors
and loss of detail due to reflection.

It cannot be overemphasized that hydrofluoric
acid is an extremely dangerous chemical capable
of producing severe burns. It is suggested that
rubber gloves be worn at all times when handling
this reagent. In addition, the acid and all appara-
tus for this development procedure must be con-
ained in an efficient exhaust hood suitable for acid.
Additional precautions and information for the
treatment of burns received from this acid may be
found on each label.

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