METHODS OF SILVERING MIRRORS.

By Heber D. Curtis.

The different processes which have been discovered for depositing a thin film of silver on glass are widely scattered in periodical literature and laboratory manuals. Some of these processes are now rarely employed, and even for the more modern methods which have proved most uniformly successful, the experience of those who have had extensive practice in silvering large mirrors will without doubt be of assistance to the amateur. The manipulation has been described by some as very uncertain and of considerable difficulty. It will be found, however, that by using pure chemicals and carefully following the directions, successful coats can nearly always be secured. Occasionally a failure will result for which no reason can be assigned. The writer has had one such experience, with the secondary mirror of the Santiago reflector, which was an absolute failure, though silvered on the same day, with the same process, and as far as was known with exactly the same manipulation which gave an excellent coat on the primary. I think that most manipulators will feel a tendency to echo the words of Quincke,—written half a century ago, it is true, when silvering processes were much less reliable than at present: "Uebrigens versagen zuweilen alle diese Methoden, oder liefern doch fehlerhafte Spiegel, ohne dass ein rechter Grund dafür aufzufinden wäre."

Siemens is said to have expressed his disbelief that any process of depositing silver from a solution could ever be discovered. Many processes have been evolved since that date, practically all of them with an ammoniated solution of nitrate of silver as a basis, the differences lying in the character of the organic reducing medium employed. Glucose, milk sugar, acidulated levulose, the juices of berries, formaldehyde, Rochelle salts, etc., have all been used. Practically all to-day use either BRASHEAR'S or LUNDIN'S methods, but some of the older methods will be given as well. The preparation of the mirror for the process is common to all methods, and will be treated first.

CLEANING THE MIRROR.

The mirror should be carefully freed from dust, and the old coat removed with nitric acid, which is also the best medium for cleaning any glass surface to be silvered for the first time. A thick swab of cotton wool is formed about the end of a glass rod, so that there is no danger of the glass rod scratching the mirror. Provided the swab is thick enough, plenty of pressure may be employed. Swab *every* part thoroughly; when the coat is all off add a little distilled water to the nitric acid already applied and go over the entire surface again. Do not let any part of the mirror become dry during the process; if any part should get dry, swab and clean again. Then rinse off the nitric acid, for which ordinary water may be used at first, followed by distilled water. Finally leave the mirror standing with a covering of distilled water over its surface; no part should be allowed to become dry.

Small mirrors may be advantageously silvered face down, resting on three thin wedges of wood cemented to the bottom of a shallow pan. For mirrors eight inches or over in diameter, however, I generally silver face up. In the case of the mirror of the Crossley reflector the preparation is as follows: The mirror is removed from its cell and supported in a ring equipped with trunnions, which allows a free tilting motion, as it is essential that the solutions be kept in constant motion during the process. A strip of paraffined paper, about eight inches wide, is drawn tightly around the edge of the mirror, leaving about six inches above the mirror. This is tied tightly with a cord. Then the paper strip is cemented to the glass by running a hot soldering-iron several times around on the outside of the paper, above and below the cord, and the overlapping ends of the paper band are cemented together in the same way. The Santiago mirror has a six-inch hole in the center; this was fitted with a wooden plug provided with a central opening and glass stopper. The plug was cemented lightly in the hole in the mirror with ROWLAND'S "Universal" wax (four parts beeswax, one part Venetian turpentine, plus a little best English vermilion). A tight joint was made with a soldering-iron, as in the case of the paper band.

After cleaning with nitric acid, many advise following with a second swabbing with a solution of caustic potash, followed in turn with an application of French chalk. I have secured better results with the nitric acid alone, and have not used the potash or chalk in recent years. On this point COMMON states: "With the most careful cleaning of a mirror, I have often found that the first application did not succeed, but the second on the surface just cleaned off with nitric acid was all right. The nature of the liquid other than distilled water last in contact with the surface of the mirror seems to be the determining thing." Dr. COMMON also preferred to silver face down when using BRASHEAR'S process, and used the Rochelle salts method when necessary to silver face up. He used a rather novel method to support the heavy mirror (37 inches in diameter; weight over four hundred pounds) when silvering face down. The back of this mirror was polished. A large cast-iron cell was made, 30 inches in diameter and about 4 inches deep; the edge was turned flat and true and then grooved; a large rubber washer was interposed between this cell and the mirror. From this cell or "sucker" the air was exhausted with a small air pump to a pressure of about 5 inches of mercury; the atmospheric pressure was then sufficient to hold the mirror to the "sucker" when face down or even when the mirror was placed in a vertical position. Considering the great weight of the glass, the method seems rather drastic. Professor WRIGHT silvered the Santiago mirror (diameter 37¼ inches; weight 562 pounds) face down on several occasions, but supported the mirror in a ring with trunnions. This mirror and that of the Crossley have a semi-circular groove about one-half inch deep around the middle of the edge, forming a safe method for support by a holding ring.

SILVERING FORMULÆ—COMMON'S PROCESS.*

Quantity used for 250 square inches (1,613 cm.^{2}) of mirror surface:

A. 1 oz. (31 g.†) silver nitrate.
10 oz. (300 cc.) water.
Clear up completely with ammonia.

B. 1 oz. (31 g.) caustic potash.
10 oz. (300 cc.) water.

Pour into A and clear again with ammonia.

Add a weak reserve solution of silver nitrate, drop by drop, till the appearance is decidedly turbid again.

C. Reducing solution:
½ oz. (15 g.) glucose.
10 oz. (300 cc.) water.

Add C to the mixture of A and B, stirring well. "At a temperature of about 56° a fine film was got in 43 minutes on the three-foot mirror. I have used some of the same solutions at various times to silver small surfaces, and I find I can get a good film in much less time, particularly if the temperature is a little higher. No doubt, for higher temperatures some modifications would have to be made; but the use of glucose allows a more certain determination of the proportions proper for certain temperatures than any mixture of sugar and acid, the active properties of which, as a reducing agent, are uncertain and changeable."

MARTIN'S PROCESS‡

1. 175 grains (11.34 g.) silver nitrate.
10 oz. (300 cc.) water.

2. 262 grains (16.98 g.) nitrate of ammonia.
10 oz. (300 cc.) water.

3. 1 oz. (31 g.) caustic potash.
10 oz. (300 cc.) water.

4. Dissolve ½ oz. (15.55 g.) sugar candy in 5 oz. (150 cc.) water; add 52 grains (3.37 g.) tartaric acid; boil for ten minutes; when cool add 1 oz. (30 cc.) alcohol; make up mixture to 10 oz. (300 cc.) in winter and to 12 oz. (360 cc.) in summer.

Mix equal parts of 1 and 2; mix equal parts of 3 and 4 in another vessel; combine when ready to silver; immediately on changing color immerse the mirror.

***English Mechanic,* **34,** 464, 1882.

†In changing these formula to the metric system, the quantities have occasionally been rounded off when it seemed evident that no error would arise thereby.

‡*English Mechanic,* **30,** 416, 1880.

ROCHELLE SALTS PROCESS (JAMES).*

1. Silvering solution:

48 grains (3.11 g.) silver nitrate.
1 oz. (30 cc.) distilled or rain water.

Add ammonia slowly till brown precipitate is nearly but not quite re-dissolved. Filter, and add distilled water to make 12 fluid drachms (45 cc.).

2. Reducing solution:

12 grains (0.78 g.) Rochelle salts.
1 oz. (30 cc.) distilled or very clean rain water.

Boil in flask, and while boiling add 2 grains (0.13 g.) silver nitrate dissolved in one drachm water. Continue boiling five or six minutes; cool, filter, and add distilled water to make 12 fluid drachms (45 cc.).

Take equal parts for silvering; temperature of 113° to 122° F. (45° to 50° C.) is best. When solution becomes clear, process is finished, taking 20 to 80 minutes; if left in longer, bleaching begins.

METHOD USED BY DRAPER.

1. 337 grains (21.83 g.) nitrate of silver.
10 oz. (300 cc.) water.
2. 1½ oz. (46 g.) caustic potash.
25 oz. (750 cc.) water.
3. 1½ oz. (46 g.) milk sugar in powder, pure and fresh.
10 oz. (300 cc.) water.

Pour nearly all of 1 into a vessel that will hold 160 oz. (5 liters),—the quantities given are for a 28-inch (71.1 cm.) mirror; add ammonia drop by drop till the gray precipitate clears; add 20 oz. (600 cc.) of 2, and with ammonia just re-dissolve the brown precipitate that forms. Make up to 75 oz. (2,250 cc.) with water, then add some of 1 till a gray precipitate that does not dissolve in three minutes is left. Then make up to 150 oz. (4,500 cc.) with water. Let it all settle, and pour off. When ready to immerse the mirror, add all of 3.

THE CROSSLEY PROCESS.

This was sent to the Lick Observatory by Mr. GLEDHILL. It was regarded as a trade secret at that time (about 1895). I find, however, that the essential part of the process was patented by PRATT in 1876, and is now generally known, forming a step in the method used by Mr. LUNDIN. There seems no longer, then, any reason why its publication should be withheld. The quantities are for a three-foot mirror.

*JAMES, quoted in *English Mechanic*, **28**, 113, 1878.

No. 1. The silver solution:

Place 7½ oz. (233 g.) of nitrate of silver in a jug; pour on it 4½ oz. (135 cc.) of ammonia (.880); stir till dissolved. Add 2½ pints (1,200 cc.) of distilled water; stir well. Filter into clean glass bottle with glass stopper. Keep in a dark place; this will keep.

No. 2. The "salts" solution:

½ lb. (250 g.) of Rochelle salt and ½ gallon (2.3 liters) of distilled water. Mix and shake till dissolved. Filter. This will keep.

No. 3. The "wash" solution:

Dissolve ½ lb. (250 g.) of crystals of protochloride of tin in 1 pint (480 cc.) of distilled water. A milky solution is obtained, with white sediment. Shake up before use. This will keep.

To prepare the solutions for silvering: For the wash take 2 drachms (7 cc.) of No. 3 and 12 pints (6 liters) distilled water. Mix well.

For the silvering solution: To each pint (liter) of distilled water add 1 oz. (64 cc.) of No. 1 and stir; then add 2 drachms (16 cc.) of No. 2 for each pint (liter), and stir.

In the use of this process all solutions should be somewhat warm. The mirror should also be warmed; this is accomplished by placing it in a large pan and pouring water into the pan a number of times, each time slightly warmer than the last, till a temperature of 100° to 120° F. (40° to 50° C.) is reached. The mirror is now tilted and the water thrown off its surface; while tilted the jug of "wash" solution is poured on the surface at the uppermost point so that a stream of the solution runs down and wets the whole of the surface. The mirror (still tilted) has now two or three eight- or ten-pint jugs of warm distilled water poured over it, no parts being missed. It is then quickly levelled and about twelve pints (six liters) of the prepared silver solution are poured upon it. If the mirror be warm enough the silver will be seen on the glass here and there in one or two minutes.

When the solution becomes discolored pour some fresh solution on (in the middle, or where any bare place is seen). Continue in this way till the coating is deemed thick enough. Then tilt mirror to throw off the discolored solution; throw over the surface a few quarts of warm distilled water; wipe surface all over with a handful of cotton wool, and tilt into vertical position to drain and dry.

This process is said to give a very good coat; I have personally seen no example of a fresh coat obtained in this way from which to judge as to its excellence and thickness, and the only trial of the method I have made (on a small mirror) gave very indifferent results, doubtless through lack of experience. When the Crossley mirror was shipped to the United States in 1895, the silver coat was found in excellent condition when the box was opened at Mt. Hamilton (silvered by the above process?). This particular coat was later used for all Director KEELER'S nebular photography, and the mirror was not re-silvered till about January, 1902. It is evident from this that the coat must have been one of unusual durability and excellence.

The function of the chloride of tin wash in this process and that used by Mr. LUNDIN is obscure. It seems essential that only the merest trace of the chloride shall be left when the silvering solutions are poured on. QUINCKE found that the slightest trace of chlorine would seriously impair the silvering process; he states that a millionth part of common salt in the silvering fluid is sufficient to make the resulting coat unfit for polishing, and advises that when only small amounts of solution are being used great care should be taken to prevent the natural perspiration of the hands from injuring the mixture.

BÖTTGER'S METHOD.*

1. Dissolve 5 grams silver nitrate in distilled water; add ammonia till the precipitate almost entirely disappears; filter and dilute to a volume of 500 cc.

2. Dissolve 1 gram of silver nitrate in a little water and pour into 500 cc. boiling water. Add to this 0.83 gram Rochelle salt, and let the mixture boil for a short time until the deposit appears gray. Filter while hot. The solutions will keep for several months in a dark place.

After cleaning the glass, pour over it equal volumes of the two solutions. The process is complete after one hour, and may be repeated to secure a greater thickness of film. The operation can be quickened by warming the *second* of the two solutions given above to 70° C. before mixing the two. Best results secured from silvering face down.

*KOHLRAUSCH, Leitfaden der prakt. Physik, 207.

BRASHEAR'S PROCESS.†

The Reducing Solution:

This should be made up in advance; the older it is the better it will work. If necessary to use a freshly made reducing solution, the action may be improved by boiling it, adding the alcohol after it has cooled. The formula is as follows:

Rock candy, 90 grams.
Strong nitric acid (spec. gr. 1.22), 4 cc.
Alcohol, 175 cc.
Distilled water, 1,000 cc.

The Silvering Solution:

(The quantities are as used for the Crossley mirror.)

A. 3 liters distilled water.
250 grams silver nitrate.
Strongest ammonia, as may be needed.

B. 1 liter distilled water.
125 grams caustic potash (purified by alcohol).

C. 25 grams silver nitrate.
200 cc. distilled water. Reserve solution.

In solution A, after the silver nitrate is all dissolved, add ammonia gradually; the solution at once turns dark brown. Keep on adding ammonia, in quite small quantities toward the close till the solution just clears up; avoid an excess of ammonia. Then pour in solution B. The mixture will again turn dark brown or black. Again slowly add ammonia, as before, till the solution just clears. The solution should now be a light brown or straw color, but transparent.

Now add as much of the reserve solution, C, as the mixture will take up without turning too dark; add this reserve solution rather slowly, stirring constantly. If 25 grams is not enough, add more, for it is important that the nitrate be as much in excess as is possible. It is best to add this reserve solution till there is quite a little brown suspended matter which the solution refuses to take up. Filter through absorbent cotton to remove these suspended particles.

Operations should be performed at a temperature of 65° to 73° F. (17° to 23° C.). If the solutions are much warmer than this, the resulting coat may be very soft, and there is, moreover, danger of the formation of some light gray silver

†*Astrophysical Journal,* **1,** 252, 1895.

fulminate, very explosive. Dr. BRASHEAR uses ice to keep the temperature below 70° F. in warm weather. If the solutions are too cold, it will be difficult to secure a coat of sufficient thickness.

Clean several drinking glasses or beakers with nitric acid, rinsing with distilled water. Make several tests of the completed solution, taking of the reducing solution one fifth or one fourth of the quantity of silvering solution employed. Note approximately the time required to get a thick coat and what proportions of reducing solution works best. Too much reducing solution gives a black, dirty coat. I generally find that about 800 cc. of reducing solution is best for the amounts given above for the Crossley mirror, and that the process is complete in from five to ten minutes.

The mirror, fitted with a band of paper as described earlier, and cleaned, has about four liters of distilled water standing upon it. Pour 800 ± cc. of reducing solution into the silvering solution, and pour at once into the water already on the mirror. Keep the solution in motion by rocking the mirror, but avoid letting any part of the mirror be exposed to the air for longer than a second or two to observe progress.

The great trouble with the Brashear process is the formation of much sediment, and the solution should be kept constantly in rapid motion so that this sediment does not remain long in any one spot. For this reason some have preferred to silver face down. Dr. COMMON on one occasion very successfully silvered his five-foot mirror face up by this process, omitting the potash, when the silver was deposited from a nearly clear liquid, leaving no mud on the surface. This procedure, however, has been very uncertain, in my hands, and the coat thin. For avoiding the sediment I find the following procedure better: Two persons, provided with rubber gloves, stand on opposite sides of the mirror, and each has, on a clean sheet of paper within easy reach, four or five good-sized handfuls of absorbent cotton. About one minute after the solution is poured on, and as soon as a bright coat begins to form, each person takes a handful of the cotton and swabs his half of the mirror very rapidly, but very lightly. No pressure is exerted, but the wet cotton is allowed to move over the surface with only its own weight. *Every* part of the mirror must be touched by the cotton. By this process the solution is kept in rapid motion, and most of the sediment is taken up by the cotton. Every half minute or so the used cotton is slightly squeezed, thrown away, and a fresh handful taken.

A difficult point is the decision as to when the process should be stopped. If the solution is thrown off too soon, the coat will be thin; if left on too long, a whitish bleach deposits, and no amount of burnishing will make such a bleached coat as brilliant as one correctly deposited. One may be guided by the time taken for the preliminary tests made on beakers, or tilt the solution slightly to one side and look through from beneath at a window or other opening. A thick coat is better in every way, particularly from its ability to stand repeated burnishings.

When completed, get the spent solution off as quickly as possible, tear off the paper strip, dash with ordinary water and then with distilled; swab the surface lightly with wet absorbent cotton if there is much "bloom" on the surface (I generally omit this); turn on edge to dry. After an hour the coat is ready for burnishing.

LUNDIN'S METHOD.*

The mirror is cleaned in the usual way with nitric acid. After the nitric acid has been rinsed from the mirror, the surface is then ready to receive a thorough rubbing with a saturated solution of tin chloride, which can best be done by making up a large wad of cotton, and holding the same in the hand so that the fingers cannot come in contact with the glass surface.

To test the surface for freedom from grease spots, etc., rinse off the tin chloride solution, rubbing the surface all the time; first with the same wad of cotton, and lastly with one or two clean wads. This will prevent the tin chloride from leaving a hard, thin film, which might otherwise form on the surface and give a granular appearance to the silver coat.

If the cleaning has been properly done, the surface after rinsing should not shed water as does a greasy surface, but should be able to retain a film of water over the entire surface when slightly inclined, and care should be taken to keep the

*Extracts from a letter from Mr. C. A. R. LUNDIN, JR., of ALVAN CLARK & SONS, to the writer.

entire surface covered with water; otherwise the silver will not deposit properly on those parts that have been exposed to the air.

A dish is formed with the mirror as bottom by wrapping tightly around the edge a strip of bandage cloth three inches in width that has previously been saturated with melted beeswax, and carefully pulled while hot from the beeswax between metal rods to remove the excess of wax which would otherwise prevent a water-tight contact with the edge of the mirror. The rim of waxed cloth can be held sufficiently tight to the edge of the mirror by a few turns of strong string and, after tying securely, wetting the same.

Having completed the above preparation, attention may be turned to preparing the silvering and reducing solutions, at the same time occasionally pouring off the water from the mirror and replacing it with a fresh supply. The total amount of solution required for silvering can now be ascertained by measuring the amount of rinsing water that it takes to cover the surface in its highest part by about three quarters of an inch.

Silver solution: Dissolve 10 grains (2.16 g.) of silver nitrate for each ounce (100 cc.) of silver solution used; add strong ammonia and clear up fully.

Reducing solution: 20 minims (4 cc.) of Merck's formaldehyde in five times its volume of water for each ounce (100 cc.) of silver solution used.

The solutions having been prepared, the water covering the mirror is now poured off, the silver and the reducing solutions are mixed quickly but thoroughly and poured into the mirror as evenly as possible. Rock the dish slowly in different directions and watch for the appearance of black grains similar to gunpowder. When the solution is clear with the exception of these particles and they seem to deposit on the silver coat, pour off the solution and rinse with running water. Remove the waxed band, all the time keeping the surface flooded with water. The remaining particles and the dull-looking deposit on the silver may now be removed with a clean wad of cotton, trailed over the wet surface without pressure.

The advantages of this process are the practically complete freedom from the troublesome sediment of the Brashear process and the possibility of using ordinary water instead of distilled. Mr. LUNDIN states that the water from the mains at Cambridge is equal to distilled water for the purpose, and would advise others to test their water supply on a small mirror before securing distilled water. The water for the cleaning should be lukewarm, and a trifle less for the solutions; should the silvering solution turn a muddy brown color when poured on the mirror, the temperature of the mirror is too high. Dr. PARKHURST writes that he finds the LUNDIN process more convenient and reliable than the BRASHEAR or the Rochelle salt method. In his opinion, the most important step appears to be the rinsing off of the chloride of tin with warm water, as all traces of the chloride must be removed to give a good film.

BURNISHING.

Make two rubbers of best chamois skin, stretched over balls of absorbent cotton. Go over the entire surface in circular strokes, first with a plain rubber to harden the film. Then grind a little best optical rouge into the chamois of the other rubber, and repeat. Dust mirror frequently during polishing, and occasionally run the edge of a knife over the pads to "scruff" them up; then dust the pads with a camel's hair brush to prevent the solid particles of rouge from making scratches. With a perfectly deposited coat only a few touches with the rouged pad will be necessary.

Of the methods given above, BRASHEAR'S is probably the most used. The writer has always used this method in silvering the mirrors of the Mills reflector at Santiago and the Crossley reflector. Properly applied, it gives a very thick, bright, and tough film, which will stand many burnishings. Dr. RITCHEY, of Mount Wilson Solar Observatory, prefers it also to any of the other processes which he has tried, and states that films deposited by this method on the small mirrors of the 60-inch reflector have remained in perfect condition as long as eighteen months with occasional reburnishing. A good coat at Mount Hamilton should last at least nine months.

Dr. SCHLESINGER uses BRASHEAR'S process at Allegheny, essentially as given above. The mirror is not removed from the telescope, and the solution is kept in motion by rocking the telescope back and forth in right ascension. He finds it essential to dry the mirror quickly after the silver has been deposited; for this purpose he employs an electric fan, and does not attempt to silver unless the atmosphere is tolerably dry. He writes:—

"For burnishing we use chamois and rouge or a good grade of absorbent cotton and rouge. Occasionally we have secured coats that are beautifully bright without burnishing, but even in these cases we have found it desirable to burnish at once, as the life of the coat is thus prolonged.

"In our situation we silver the 30-inch mirror once a month and the secondary (hyperboloidal) mirror every two weeks. In the violet and ultra-violet portions of the spectrum the mirrors decrease considerably in effectiveness only a few days after they have been renewed.

"When the mirrors are not in use they are protected by metal covers lined with absorbent cotton. The latter is pressed into contact with the silvered surfaces and effectually prevents the oxidation that would otherwise rapidly spoil the silver.

"Although the tube of the telescope is entirely open and the mirrors are thus directly exposed to the heavy dew that we occasionally have here, we have never noticed the least deposit of moisture on the mirror. Care must be taken, however, not to expose the mirrors when they are colder than the air, as in that case the moisture immediately condenses on the silver and seems to get between it and the glass."

The air at Mount Hamilton is of course almost absolutely free from deleterious vapors which would injure the film, so such frequent silverings have not been found necessary. The flap which covers the mirror of the Crossley is about three feet above the mirror, but is never closed in the summer time; the mirror is occasionally dusted with a very soft, fine feather duster to clean off the light dust which gradually collects on the surface.

In some localities the deterioration of the silver coat is so rapid that considerable thought has been given to methods for protecting the film. A method due to M. IZARN* consisted in coating the mirror with a thin film of bichromatized gelatine, and was tried with some success at the observatory of Toulouse.

Comptes Rendus*, **118, 1314, 1898.

Perot* describes the method of forming a very thin film of celluloid over the silver film:—

"After having thoroughly washed, dried, and polished the mirror, and having very carefully removed all dust, a dilute solution of celluloid in amyl acetate is poured over the surface. The operation can be performed at ordinary temperatures, and the commercial solution, known as Japan varnish, diluted with about its volume of amyl acetate, serves very well. The mirror is tilted so as to let the excess drain off and is dry in half an hour. Broad, strongly colored interference bands (colors of the third order) should then be seen on the surface, showing that the uniform thickness of the celluloid is about 0.5 μ. Under these conditions the images are bright, sharp, and show no diffusion if the film of celluloid is thin. The results obtained at the observatory of Meudon from the use of this varnish are very favorable. Among others, a plane mirror 60 cm. in diameter, which formerly had to be silvered every month in the year, lasted nearly six months, and without doubt could have been used longer if the washing after silvering had been made with greater care. The protecting coat is rather soft, and care should be taken to avoid scratches. The dust which gradually collects on the surface should be removed by a very gentle dusting."

All silvering processes appear to be very wasteful. Dr. Common removed a fine coat from his five-foot mirror after a year's use. On weighing, the thickness of the silver film was found to be 1/280,000 of an inch = 907 tenth-meters. Of the 400 grams of nitrate of silver used in depositing the film only 1.7 grams was laid down as silver.

Chloride of silver can be deposited from the spent solutions by the addition of common salt, and the silver thus ultimately recovered.

A thick film will have a much longer life than a very thin one. Quincke states that he silvered a small mirror with a very thick coat (Petitjean's process, employing tartaric acid as reducer) which stood one hundred and fifty reburnishings.

A convenient way of determining the thickness of a silver film is due to Fizeau.† "To determine the thickness of the

Comptes Rendus, November 2, 1909.

†*Comptes Rendus,* **52,** 274, 1861.

deposit of silver a bit of iodine was placed on its surface, and allowed to develop about it, under the influence of its emanation, colored rings of silver iodide till the spot occupied by the iodine became entirely transparent, the silver coat at that point being transformed into yellow iodide through its entire thickness* From the point where the vapors of iodine had not touched the silver up to that where the metal was entirely transformed into iodide, there was a series of colored rings beginning with white and which, counted with a red glass, were found to number nine. The series ceased about the middle of the ninth bright ring. The index of refraction of silver iodide being 2.246 . . . , the ninth bright ring gave for the thickness of the silver iodide 0.001193 mm. Thence was derived 0.000294 mm. for the thickness of the silver coat."

FIZEAU describes this film as "very thin, but nevertheless of perfect opacity." It was certainly a very thick film and more "massive" than is ordinarily secured. Another film, which he describes as opaque to light of moderate intensity only (silver foil) gave NOBILI'S rings to the fourth bright ring, corresponding to a silver thickness of 1,102 tenth-meters; the Sun could be seen through this film, colored a very rich blue. A still thinner film of a greater degree of transparence showed the iodide rings to the second bright ring, corresponding to a thickness for the silver film of 367 tenth-meters.

For the use of this method, the following table will suffice:—

THICKNESS OF THE ORIGINAL SILVER FILM AS DETERMINED FROM NOBILI'S RINGS IN SILVER IODIDE.

To first dark ring			180	tenth-meters
" second bright ring			370	" "
" third	"	"	740	" "
" fourth	"	"	1,100	" "
" fifth	"	"	1,470	" "
" sixth	"	"	1,840	" "
" seventh	"	"	2,200	" "
" eighth	"	"	2,570	" "
" ninth	"	"	2,940	" "
" tenth	"	"	3,300	" "

*For the symmetrical production of these rings (known as NOBILI'S rings) it is well to avoid the effect of air drafts by placing a funnel or beaker, which should not fit too closely to the surface, over the crystal of iodine.

The color of the silver transformed to silver iodide may instead be determined by reflected light. If e is the thickness of the air film which would show the same Newtonian color as that given by the silver iodide film, then from

The atomic weight of silver	= 107.9 = Ag
The atomic weight of silver iodide	= 234.9 = IAg
The specific gravity of silver	= 10.55 = d
The specific gravity of silver iodide	= 5.6 = d′
The refractive index of silver iodide	= 2.15 = n

the thickness of the silver film from which the silver iodide was formed is—

$$D = \frac{Ag}{IAg} \cdot \frac{d'}{d} \cdot \frac{e}{n} = 0.114\, e$$

Thence we have the following table, adapted from DRUDE'S table in *Wied. Ann.*, **50**, 607, 1893; the colors are QUINCKE'S:—

TABLE FOR DETERMINING THICKNESS OF SILVER FILMS.

Thickness of original silver film in tenth-meters.	Colors of silver iodide film in perpendicularly reflected white light.	
0	Black	First Order
38	Iron gray	
56	Lavender gray	
94	Bluish gray	
112	Clear gray	
146	Greenish white	
167	Straw color	
186	Bright yellow	
223	Sorrel	
261	Reddish orange	
279	Warm red	
298	Deeper red	
317	Purple	Second Order
336	Indigo	
373	Sky blue	
410	Greenish blue	
429	Green	
467	Clearer green	
484	Yellowish green	
503	Greenish yellow	
521	Pure yellow	
540	Orange	
577	Reddish orange	
615	Dark violet red	

TABLE FOR DETERMINING THICKNESS OF SILVER FILMS (Continued).

Thickness of original silver film in tenth-meters.	Colors of silver iodide film in perpendicularly reflected white light	
652	Clear bluish violet	Third Order
671	Indigo	
708	Blue (greenish)	
746	Sea green	
783	Brilliant green	
821	Greenish yellow	
840	Flesh color	
877	Carmine red	
914	Dull purple	
933	Violet gray	
952	Grayish blue	Fourth Order
971	Dull sea-green	
989	Bluish green	
1026	Fine pure green	
1101	Clear gray-green	
1139	Gray, almost white	
1157	Flesh red	

A still more accurate method of determining the thickness of the silver film was employed by DRUDE in the paper quoted, but requires some subsidiary apparatus and would be very difficult of application to a surface not plane. The film is transformed into iodide by FIZEAU'S method and a narrow strip of the iodide is then scratched off. A plane glass plate is then placed over the film so as to make a very thin prism of air whose refracting edge is perpendicular to the direction of the strip. The interference fringes thus produced by homogeneous light show a shift where they pass over the strip freed from iodide, and from the magnitude of this shift the thickness of the original silver film can be very accurately determined.

CONROY, with a film 845 tenth-meters thick, states: "The film appeared opaque by ordinary daylight, but when examined with sunlight was seen to be slightly transparent and of a deep blue color." Double silvering gave a film 1737 tenth-meters thick. "This film was not absolutely opaque as the disk of the Sun on a clear day could be just seen through it, but it transmitted much less light than the film previously used."

The amount of light reflected from silver films has been determined by a number of investigators, though there is some difference in the results secured. As is well known, silver is more or less transparent to the ultra-violet rays, as may be illustrated by the following data as to the percentage of light reflected at perpendicular incidence, taken from LANDOLT und BÖRNSTEIN'S Physikalisch-Chemische Tabellen:—

Wave lengths.	Per cent reflected.
λ 3050	9.1
3160	4.2
3260	14.6
3380	55.5
3570	74.5
3850	81.4
4200	86.6
4500	90.5
5000	91.3
6000	92.6
7000	94.6
8000	96.3

LANGLEY found the following values:—

Wave lengths.	Per cent reflected.
λ 3500	61
3800	73
4000	79
4500	85
5000	89
5500	91
6000	93

Much naturally depends upon the freshness and condition of the film. SCHLESINGER states that a good coat will reflect about 85 per cent of the incident light at λ 4860, and about 70 per cent at λ 3934.

The amount of reflectivity as depending upon the thickness of the film has never been adequately investigated, though much work has been done on the other optical constants of silver in films of different thickness.

Sir J. CONROY has made some related investigations on this point.* He used MARTIN'S process for depositing the films. "The room in which the silvering was carried on being very cold, the action was slow, and till at least five minutes had elapsed there was hardly any deposit; the slips were removed successively after 8, 11, 14, and 18 minutes, well washed with

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water and placed on edge to dry." By weighing the glasses with and without the films the thicknesses were calculated as follows:—

Film	I,	removed after	8	minutes,	thickness	404	tenth-meters		
"	II,	"	"	11	"	"	685	"	"
"	III,	"	"	14	"	"	772	"	"
"	IV,	"	"	18	"	"	900	"	"

His results indicated that the optical constants of a polished silver plate depended to a certain extent upon the substance with which it had been polished, and that this surface condition was a fairly permanent one, not being destroyed by contact with liquids or by a considerable amount of rubbing with a clean chamois leather. He found in particular that a film polished with rouge had a slightly reddish tinge; using putty powder instead, the principal azimuths of the reflected rays were considerably higher and differed but little for red, yellow, and blue light, whereas when polished with rouge these increased with the refrangibility of the light. He found also that the principal incidence and principal azimuth both increased with the thickness of the film, and that therefore it seemed that more than one layer of molecules was concerned in the act of reflection. This would indicate that light polarized perpendicularly to the plane of incidence penetrates to a greater depth in the film than that polarized in the plane of incidence.

The observations of WIENER and DRUDE show also that for thin films the optical constants are very different from those of "massive" silver, for the refractive index of silver in very thin films ($0.02\,\lambda = 120 \pm$ tenth-meters) is greater than unity, while it is less than unity for "massive" films, i. e. those nearly or entirely opaque ($0.1\,\lambda = 600$ tenth-meters).

As is well known, silver appears under a number of allotropic forms, three of which have long been recognized,—namely, crystalline silver (tree-formed crystals), "mirror" silver, and granular or powdered silver. In addition to these there are a number of other interesting allotropic modifications produced by special methods,—silver possessing the yellow color and luster of gold, another like copper, and others brown and green. These allotropic modifications possess the curious property that the powdered moist mass may be spread upon a surface with a brush and when dry they possess the characteristic metallic reflecting power and are apparently as coherent and unbroken as a film deposited in the ordinary way. All these forms are somewhat unstable, and the gold-colored silver and the copper-colored variety soon change into ordinary mirror silver under the action of light or of a moderate degree of heat. I have had test films on beakers which were so golden in appearance that it seems certain that a portion of the coat at least was the gold-colored allotropic variety. Considerable work has been done on these allotropic forms.*

OBERBECK found that the electrical resistance of chemically deposited silver films decreased greatly with time. This change was quite rapid for the first few days, becoming slower later, and was still decreasing slowly after 641 days, when the electrical resistance averaged only about 15 per cent of that of a freshly deposited film. He used BÖTTGER'S method, and it was his opinion that a considerable portion of the freshly deposited film was an allotropic modification of ordinary "mirror" silver. LÜDTKE corroborated these results for mirrors silvered by the same process, and also for mirrors silvered by DRAYTON'S and PETITJEAN'S methods. Mirrors silvered by LIEBIG'S and MARTIN'S processes, however, showed no such decrease in resistance with the time. All these investigators state that the outward appearance of the mirrors remained the same, but it is unfortunate that none of them appear to have carried on tests of reflectivity at the same time with the electrical tests. The decrease was quickened by the direct action of sunlight, just as in the experiments made with allotropic forms the change to ordinary mirror silver was similarly hastened. The suggestion has been made that the bleach seen on a mirror left too long in the silvering solution is the granular powdered form of silver.

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*VOGEL, *Pogg Ann.*, **117**, 316, 1862; OBERBECK, *Wied. Ann.*, **46**, 265, **47**, 353, 1892; LÜDTKE, Ueber die Eigenschaften verschiedener Silbermodificationen, Inauguraldissertation, Greifswald, 1893, and *Wied. Ann.*, **50**, 678, 1893; CAREY LEA, *Amer. Jour. of Science*, **37**, 476, **38**, 47, 237, 1889, *Phil. Mag.*, **31**, 238, 321, 497, **32**, 337, 1891.