

Rapid Processing of Photographic Plates for Routine Spectrographic Analysis¹.

by

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With 3 figures in the text.

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Since the casting of alloy iron is usually a continuous rather than a batch process, the problem of composition control resolves itself into a control of the drifts in the concentration of the several alloying constituents in the molten iron in the furnace or cupola. If the drifts are to be maintained within narrow limits of tolerance, the analysis system used must meet several requirements. The accuracy of the analysis must, of course, be adequate; specifically, the uncertainty must be substantially less than the permissible variation in content. In addition, it is of vital importance that the elapsed time between the pouring of a sample of the iron and the posting of the analysis results should be made as brief as possible; otherwise, a control of drifts is not provided and an inspection analysis only results.

For some years, the authors have been interested in the application of the spectrograph to routine control problems in iron and steel. Papers have been published elsewhere²⁻³ on the development of a spectrographic method of analysis and its installation at the plant of the Campbell, Wyant and Cannon Foundry Company, Muskegon, Michigan. The procedure permits the analysis of a sample of cast iron for chromium, copper, manganese, molybdenum, nickel and silicon in seven minutes elapsed time, while the accuracy exceeds that of the routine chemical wet methods previously used.

In the analysis procedure, spectra are recorded on a photographic plate on glass sufficiently thin to accept without fracture the curvature imposed by the spectrograph. The plate is processed, and, since efforts to measure densities on wet plates have proved uniformly unsatisfactory, it is dried before the readings are taken. Since the processing and drying of the photographic plate was initially, and still remains, the most protracted operation of the analysis schedule, the problem of reducing the time required has been given considerable attention. It is thought that the technique developed may be of interest to spectroscopists and to others for whom rapid plate processing is urgent. Details of the procedure are presented below.

While the processing of any photographic plate may be hastened, it is necessary to control the emulsion thickness much more carefully than is customary for stock plates if a uniform time schedule is to be maintained. All of the

¹ The developments reported here were carried out in the Department of Physics in connection with industrial projects sponsored through the Department of Engineering Research.

² Vincent, H. B. and R. A. Sawyer: J.A.P. 8, 163—173 (1937).

³ Vincent, H. B., R. A. Sawyer and A. M. Sampson: Metals and Alloys, Feb. 1938.

plates used for routine analysis are special in that the thickness of the dry emulsion is held very close to one one-thousandth of an inch. For this emulsion thickness, in the neighbourhood of 3000 Å, the density is proportional to the logarithm of the exposure for densities between 0,2 and 1,2. If higher densities are mandatory, a thicker emulsion must be used and the corresponding increase in processing time accepted. A further requirement of the emulsion is very strong adhesion to the glass to withstand without frilling the sudden changes in concentration between solution and wash.

The plate used most extensively for analysis work has been a special Cramer Contrast plate manufactured by the G. Cramer Dry Plate Company, St. Louis,

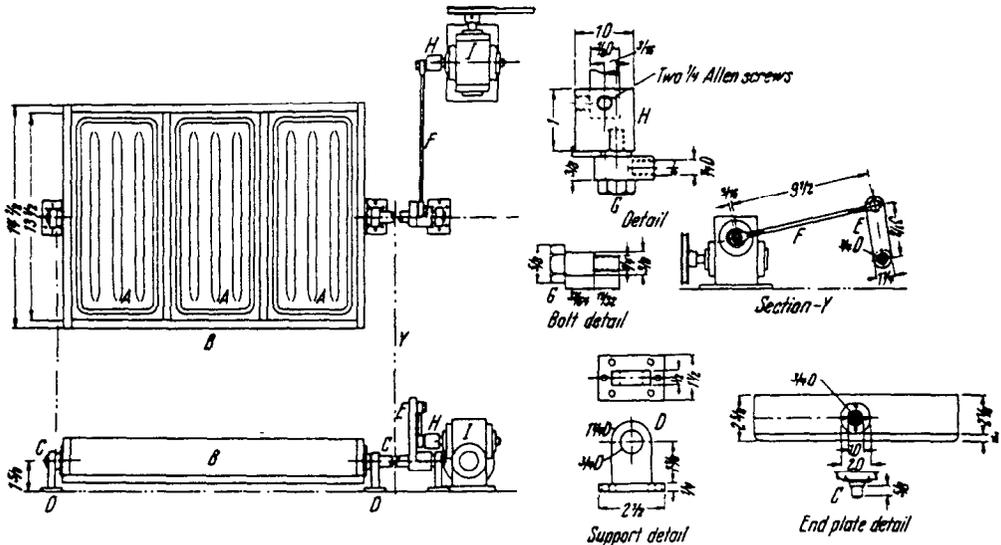


Fig. 1. Apparatus for the agitation of the processing solutions.

Mo. This plate is processed and dried in laboratory routine in an elapsed time of four to five minutes. The Eastman Kodak Company has recently developed a special Contrast Process Plate which requires about three minutes for processing and drying¹. These plates both have fine grain and high contrast. The processing described below yields a gamma of about unity.

Not only the reducing solution employed, but also the method of its application, are important if brief and satisfactory development is to be realized. If the time is quite short, of the order of one minute or less, uniform development is hardly to be anticipated with random or no agitation of the solution; under such conditions, Eberhard effect may be quite troublesome. Uniform positive agitation not only minimizes these difficulties, but has the desirable effect of hastening all phases of the processing, developing, hardening and fixing.

While the apparatus for agitation of the solutions should be adapted to the individual requirements of the laboratory, a satisfactory unit arrangement is shown in Fig. 1. Glass trays A are carried in a wooden frame B attached to shafts C supported by bearings D. The trays are oscillated about the axis C by means of arm E and rod F engaging the decentered pin G carried on the

¹ This plate is, at present, designated as No 385.

power is used briefly at the start of the process to elevate the emulsion rapidly to the drying temperature. Air from the room is driven rapidly across the emulsion by the fan *F*, a relatively feeble current of air is carried through the box by the small holes *HH* to remove the moisture evaporated from the glass surface of the plate. The depression *G* facilitates the removal of the dried plate from the dryer.

For plates four inches wide by ten to twelve inches long, the lower power input should be about 450 watts; the higher power is, of course, four times the lower. The glass, while transmitting infrared radiation which is absorbed by the water in the emulsion, also absorbs the longer wavelength rays which, together with some contribution from convection, raises its temperature during the

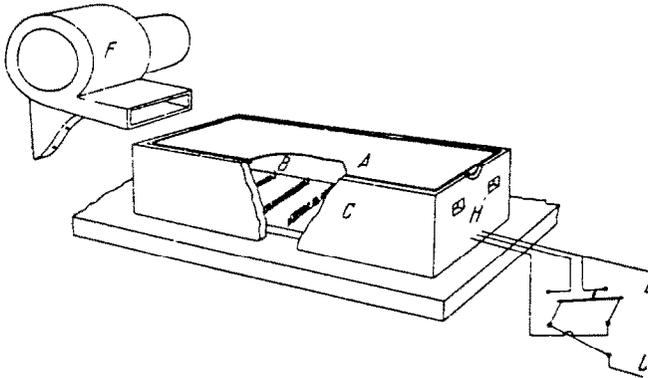


Fig. 3. The plate dryer.

drying. If the power mentioned above is used, the plates must be removed promptly when dry or the glass will probably crack.

The choice of a developing solution involves several considerations. A single solution developer is obviously preferable for routine work since the errors likely to occur in compounding under the pressure of maintaining an operating schedule are eliminated. The solution must be clean-working and have reasonable keeping qualities, although in laboratories using several dozen plates per day storage over long periods is unnecessary. Above all, the reduction potential must be high so that development proceeds rapidly.

To meet these requirements, the authors have used a hydroquinone-caustic soda developer of the type of the Eastman D8 and similar formulas. The caustic soda content or the concentration or both are adjusted to yield a minimum development time without appreciable discoloration of the unexposed portions of the plate. With the Cramer plates, batch to batch variations in characteristics have necessitated occasional readjustment of the developer formula; the limited experience with the Eastman 385 plate indicates better uniformity and less tendency toward stain. A typical developing formula is given below.

Sodium Sulphite, desiccated	60 grams
Hydroquinone	30 ..
Caustic Soda	20 ..
Potassium Bromide	20 ..
Water to make	1 liter

Develop for 30 seconds at 70° F.

Unquestionably, higher development speeds can be realized with reducers such as pyrocatechin or catechol. However, for uniform results it appears necessary to provide a reasonable penetration time; even if the strong staining tendency of pyrocatechin could be eliminated without decreasing its activity, it is doubtful if an important saving of time could be effected. Developers containing sodium or potassium carbonate as alkali, and especially those using glycin as reducing agent, have superior keeping qualities, but with all such formulas tested, the development was prolonged. It is thought that metal shows more variation in contrast with degree of development, than does hydroquinone, — an undesirable characteristic since, for routine photometric work, constant or nearly constant contrast is advantageous.

To permit the application of relatively high temperatures in drying, the plates are hardened in a twenty per cent chrome alum solution. Formalin, while quite effective, is undesirable since its fumes are disagreeable and slightly toxic. The prehardening of the plates in manufacture may be carried to a point where further hardening during processing is not necessary, but, since the penetration of the solutions is delayed by the prehardening, the processing time is likely to be extended.

In routine analysis work, where density measurements are to be effected immediately and where ability to withstand storage over long periods without deterioration is unimportant, the plate may be removed from the fixing bath as soon as it is cleared. The clearing time is dependent on two factors, the thickness of the emulsion and the activity of the bath. Emulsion thickness has been discussed above. The formula for a fixing solution which has been found to be quite satisfactory is given below.

Sodium Thiosulphate	300 grams
Ammonium Chloride	60 "
Sodium Bisulphite	45 "
Water to make	1 liter

Some acidulation of the fixing bath is desirable since the chrome alum carried over from the hardening precipitates sulphur from a neutral solution. However, the addition of acid decreases the activity so such additions should be kept as small as feasible. Other acidulators such as potassium metabisulphite or acetic acid with sodium sulphite may be used quite satisfactorily.

It appears desirable to mention at this point a matter which, while quite obvious, is sometimes overlooked. The cost of the solutions is very moderate and the use of fresh baths of standard activity promotes uniformity in processing. The use of solutions to complete exhaustion is never justified, and, indeed, they should be replaced at the first evidence of fatigue.

Process	Photographic Plate	
	<i>Eastman</i> 353 seconds	<i>Cramer</i> Contrast seconds
Develop	30	30
Rinse and transfer	10	10
Harden	15	15
Drain and transfer	5	5
Fix	25	45
Drain and transfer	5	5
Wash	30	30
Rinse, distilled water	10	10
Sponge	10	10
Dry, high power	15	15
Dry, low power	25	75
Total	180	250

The processing schedule for plates used in routine procedure is given below. Some variation from plate to plate in the fixing and drying speed is to be anticipated; the times quoted are average. The sponging mentioned in the following table involves the removal of surface moisture from the plate by means of a viscose sponge dampened with distilled water.

The technique described above is in current use at plants of the Campbell, Wyant and Cannon Foundry Company, Muskegon, Mich., the Great Lakes Steel Corporation, Ecorse, Mich., the Bethlehem Steel Company, Lackawanna, New York, and the Ford Motor Company, Dearborn, Mich. The times cited are taken from the Ford laboratory schedule. Experience has shown that the uniformity of the processing satisfies adequately the exacting requirements of routine spectrographic control analysis. The procedure outlined and adaptations thereof are recommended for consideration where rapid processing of photographic materials is advantageous.