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A contribution to the study of the photometric equivalent of sensitive photographic layers

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A CONTRIBUTION TO THE STUDY OF THE PHOTOMETRIC EQUIVALENT OF SENSITIVE PHOTOGRAPHIC LAYERS

PŘÍSPĚVEK KE STUDIU FOTOMETRICKÉHO EKVIVALENTU FOTOGRAFICKÝCH CITLIV|ÝCH VRSTEV

К ВОПРОСУ ИЗУЧЕНИЯ ФОТОМЕТРИЧЕСКОГО ЭКВИВАЛЕНТА ЧУВСТВИТЕЛЬНЫХ ФОТОГРАФИЧЕСКИХ ПЛЕНОК

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INTRODUCTION

The course of development is not usually studied directly by the determination of the concentration of deposited silver in a photographic layer, but by one of the following three indirect methods:

(i) the determination of optical density of deposited silver,
(ii) the analytical determination of the concentration of oxydation products of the reducing agent,
(iii) the determination of the concentration of released halogen ions in the developer.

For the indirect methods the dependence of the studied quantity on analytic concentration of deposited silver must be known.

When the dependences of analytic concentration of oxydation products in the developer[1] and of optical density[2] on concentration of depositied silver in the sensitive layer were compared, it was found that these relations were not the same at all occasions. In order to explain the discrepancies work was started on a detailed study of the relation between the optical density and the concentration of deposited silver i. e. the study of the photometric equivalent.

The relation between the concentration of deposited silver and optical density was studied earlier by Hurter and Driffield[3]. They found that the ratio $C_{Ag}/D = P$ (1) a constant — they called it the photometric constant (C_{Ag} is the concentration of deposited silver, D the optical density). Later it was found that P is not constant, but that it depends on the type of photographic material, on exposure of the emulsion and on development time. From Nutting's[4] expression for the optical density

$$D = \frac{N\bar{a}}{2.3} \qquad (2)$$

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(N is the number of developed grains per square centimeter, $\bar{a}$ the average projection area of a grain) it follows, that the photometric equivalent is a linear function of the average radius of the developed silver grains. ARENS, EGGERT and HEISENBERG[5] came to the same conclusion. EGGERT and KÜSTER[6] found the relation between the photometric equivalent and the average diameter of the developed grain.

$$P = 1.53\bar{d} \cdot \varrho \tag{3}$$

where $\bar{d}$ is the average diameter of the developed grain and ϱ the "effective" specific gravity. The above authors presumed, that the silver in the developed emulsion is compact. Research conducted with an electron microscope on the shape factor of grains in developed sensitive layers revealed that this supposition is not fulfilled. Klein[7], who studied the effect of the distribution of grains according to size in the emulsion found the density to be

$$D = \frac{1}{2.3 S_{Ag}} \cdot \frac{M}{\bar{d}} \cdot \frac{\dfrac{0.391}{h_d^2} + \dfrac{\pi}{4}\bar{d}^2}{\dfrac{0.786}{h_d^2} + \dfrac{\pi}{6}\bar{d}^2} \tag{4}$$

(where S_{Ag} is the density of deposited silver, M is the mass of silver, $\bar{d}$ is the average diameter of the developed grain a h_d is the covering power). This expression gives the dependence of the photometric equivalent on the size-distribution of emulsion grains as well.

Some of these results were not known to SHEPPARD and BALLARD[2], who studied the photometric equivalent and therefore the aim of this work is to control and complete their results and explain the causes of the found discrepances.

EXPERIMENTAL-PART

The dependence of the photometric equivalent on optical density D, on exposure E, on development time t, on temperature T of developer and on type of developer was studied for two sensitive materials:

   (i) negative unsensibilised material Agfa Tf4, sensitivity 11/10 DIN,

   (ii) negative fine grain material Agfa Isopan FF, sensitivity 10/10 DIN.

Sensitometric strips were exposed on Bouček's film sensitometer. The intermittent exposure was attained by sectors, whose area rose by steps of $\sqrt{2}$. The modulation constant was 0.15 and the scale of exposure was 1 : 256. The light from the source of colour temperature 2850° K passed through a rolating arm and exposed successively 17 apertures for a time of 0.75 sec. The illuminance of the film through the largest aperture was 32 lx. The size of the film window was 16 × 22 mm.

The sensitometric strips were developed in ferro-oxalate, fenidon and Kodak D 76 developers. The strips were fixed in a fixing bath containing ammonium
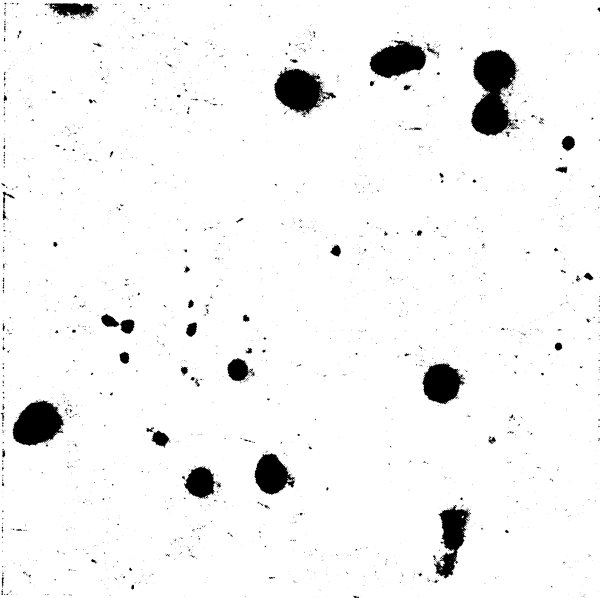
Fig. 1. Photograph showing emulsion grains of negative material Agfa Isopan FF, sensitivity 10/10 DIN (magnified 14000×).
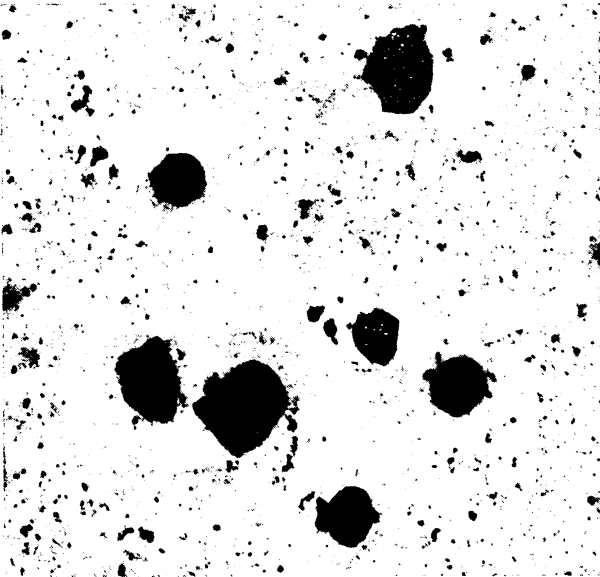

Fig. 2. Photograph showing emulsion grains of negative material Agfa Tf 4, sensitivity 11/10 DIN (magnified 14000×).

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chloride. The measurement of optical density was made on a photoelectric densitometer RFT.

For the determination of the concentration of silver per unit area a sample of 1.3 square centimeters was cut from each field of the strip. The size of samples was controlled by weighing on an analytical balance and samples differing by not more $\pm$ 1 % in weight were used. In these samples the mass of silver was determined by a potenciometric method, which, according to preliminary experiments, showed itself to be more reproducible than the so far used colorimetric method. From these results the values of the photometric equivalent were calculated.

In order to confirm the results gained from the study of the dependence of the photometric equivalent on the above cited conditions it was necessary to
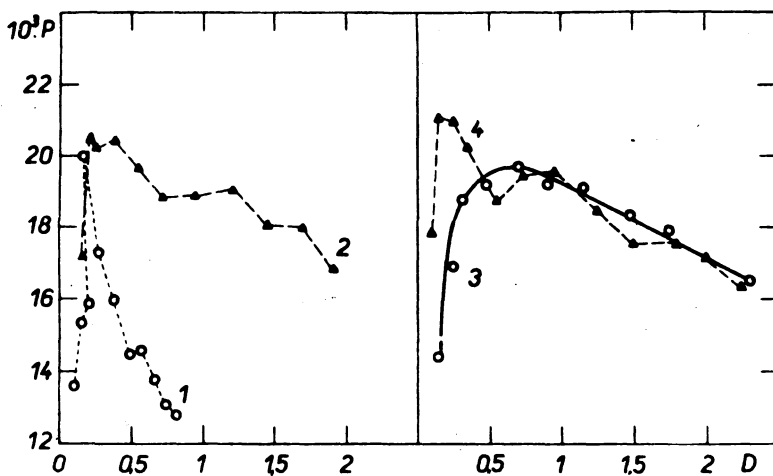

Fig. 3. Graph of P/D for material Agfa Tf 4 (sensitivity 11/10 DIN) developed in an inorganic ferro-oxalate developer. Development times: 1—2 min., 2—8 min., 3—12 min., 4—20 min.

show, that the sensitive layers used in the experiments not only differ greatly in size and shape of grains but in their distribution as well. Further by developing the layers under diferent conditions, silver grains of different size were gained. Their size and shape depends on the amount of light energy transfered during exposure and on duration and temperature of development.

Microphotographs of unexposed and undeveloped grains of both tested photographic materials were made on an electron microscope (fig. 1, 2). Photographs from an optical microscope were made to show grains developed under diferent conditions.

The dependence of the photometric equivalent on optical density

The dependence of the photometric equivalent P on optical density D for exposed and developed samples was studied both on the unsensibilised Tf 4

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material of 11/10 DIN sensitivity and on the negative Isopan FF material of sensitivity 10/10 DIN. The dependence of P on D for unexposed but developed samples (i. e. the relation between P and the density of fog D_0 for different development times) was studied only on Tf 4 material.

By comparing the results shown in fig. 3, 4, 5, 6 it can be seen that the dependence of the photometric equivalent on optical density is influenced not only by the properties of the material but also fundamentaly by the reducing agent used in the developer and by time of development. The influence of the development time on the variation of the dependence of P on D which was studied on Tf 4 material is shown in fig. 3. For short-time development (2 minutes), the photometric equivalent depending on optical density rises, reaches a maximum value and then falls. When the development time is prolonged the steep rise of the photometric equivalent remains the same for small optical densities, but further the values of P in dependence on optical sensitivities (related to the linear part of the curve) are rather different. The curves show the presence of "maximas". For long development times the "maximas" disappear and the curve becomes of normal form. The form of the curve P/D which was obtained by development in developers with organic reducing agents (fig. 4) is similar to that obtained by development in an inor-
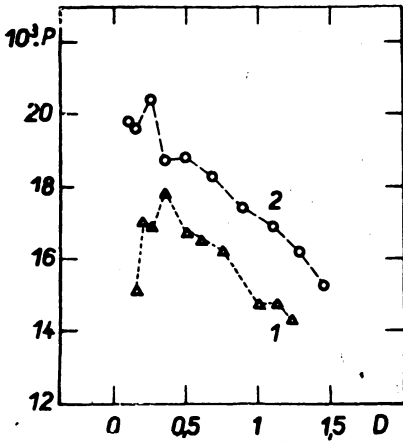

Fig. 4. Graph of P/D for material Agfa Tf 4 developed in developers with organic reducing agents. Curve 1: fenidone developer, curve 2: Kodak D 76 developer.
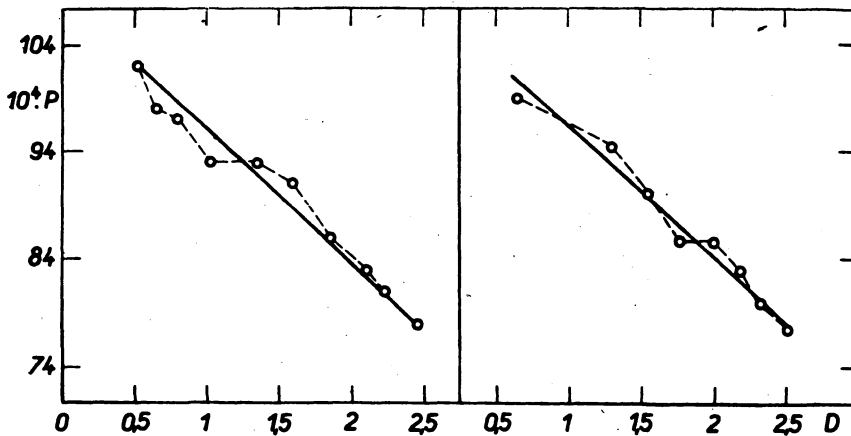

Fig. 5. Graph of P/D for material Agfa Isopan FF developed in an inorganic ferro-oxalate developer. Development times: curve 1 : 5 min., curve 2 : 10 min.

ganic ferro-oxalate developer. The values of the photometric equivalent that refer to given optical densities are however different.

The variation of the dependence for negative Isopan FF material (fig. 5) is much simpler and the form of the curve for development time of 5 and 10 minu-
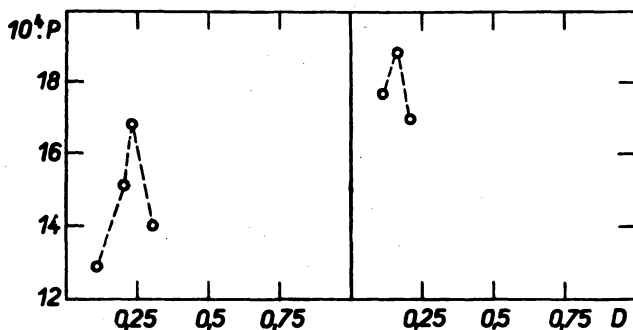
Fig. 6. The relation between the photometric equi-
valent and optical density obtained for developed
unexposed material Tf 4.
Curve 1: ferro-oxalate developer, curve 2: Kodak D 76
developer. (The individual points on curve 1 represent
development times of 20, 40, 60, 80 min. — on curve
2: 20, 40, 60 min. resp.)

tes is almost identical. Any rapid rise in the photometric equivalent is not apparent in the curves for low values of optical density and the curve shows no "maximas". The curve is monotone. The value of P is lower by an order then for Tf 4 materials.

Fig. 6 shows the variation of the photometric equivalent with the density of fog, i. e. with the optical density of unexposed developed Tf 4 material. The developing was carried out in an inorganic (ferro-oxalate) developer as well as in a developer with anorganic reducing agent (developer Kodak D 76). The microphotographs (fig. 7, 8) show, that there is not much difference in size and shape of the grains forming fog and those related to small optical densities gained by development of an exposed sensitive layer.

Changes in the form of P/D curves produced by the lengthening of develop-ment time can be explained by the fact, that for short development times, the only grains that are developable are those which gained sufficient energy at exposure — mainly large grains whereas for longer development times all the grains are practically developable (clumping of grains takes place). The pre-sence of the "maximas" is probably produced by singular reduction, which more influences a material with a large size-distribution of grains than materials Tf 4, where the size-distribution of grains is smaller.

The higher value of the photometric equivalent for low values of log E and of optical densities supposes that for short development times the large grains are mainly developed — for higher values of log E and optical densities, the value of the photometric equivalent falls, because for longer development
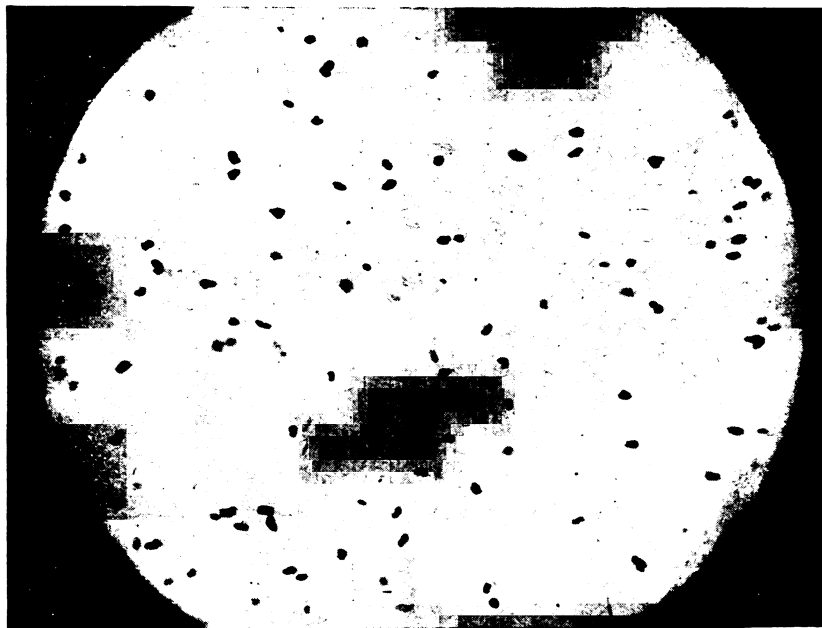
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Fig. 7. Microphotograph showing developed grains of unexposed material Agfa Tf 4. (Optical density of fog is 0.1, ferrooxalate developer, development time 20 min.) Total magnification is 5400.

times smaller grains become developable. The lower value of the photometric equivalent for a fine-grain material (10/10 DIN) can be explained by the smaller size of reduced silver grains in comparison with the size of grains for Tf 4 material (fig. 9, 10).

The dependence of the photometric equivalent on the logarithm of exposure

The dependence of the photometric equivalent on the logarithm of exposure is very similar to that on optical density (fig. 11, 12, 13). If we follow the dependence of the photometric equivalent on the logarithm of exposure for short development times (2 minutes) (fig. 11) on Tf 4 material, we can see that the photometric equivalent rises to larger values for longer exposures — for a definite value of $\log E$ it reaches a maximum and again falls. For longer development times similarly as in the case for P/D the variation of the dependence becomes more complicated (a simple curve cannot be passed through the experimental points) — "maximas", which fade away after long development times where the curve is "normal", begin to appear.

The dependences $P/\log E$ studied on the Tf 4 material developed in organic fenidone developers and Kodak D 76 (fig. 12) differ from the studied dependences P/D only in the values of the photometric equivalent.
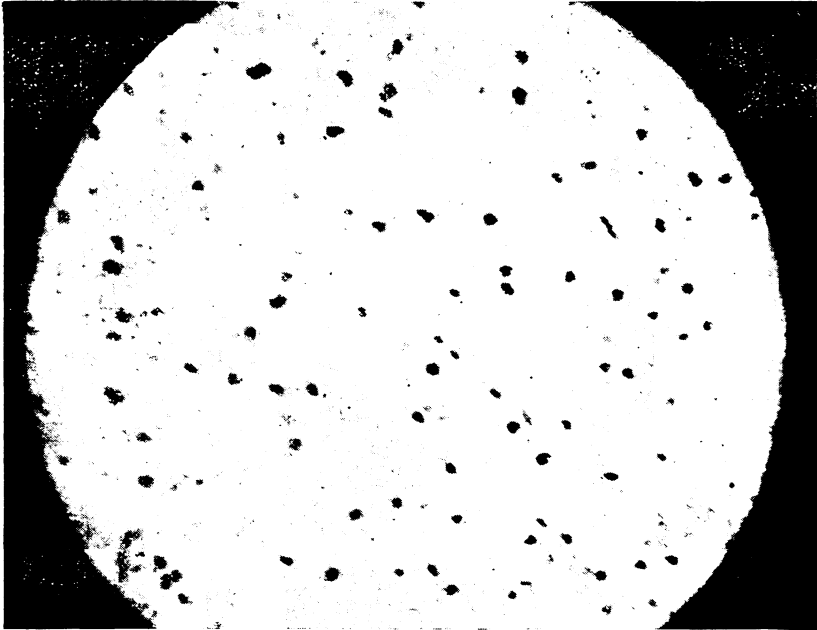
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Fig. 8. Microphotograph showing developed grains of exposed material
Agfa Tf 4. (Optical density of sample is 0.24, ferro-oxalate developer,
development time t = 20 min., log E = —0.125 1× sec).
Total magnification is 5400

For Isopan **FF** materials the curve $P/\log E$ is simpler then for materials of medium sensitivity (fig. 13). The value of P falls smoothly—the curve shows no "maximas" and is almost linear.

The dependence of the photometric equivalent on optical density for different developing temperatures.

A ferro-oxalate developer was used to study the influence of temperature on the variation of P with D and P with log E. Four development temperatures (18, 20, 28, 38° C) were used—development time was 8 minutes. The results obtained from the temperature dependencies are shown in fig. 14 and 15.

The curves (fig. 14 and 15) show, that the photometric equivalent radically changes with development temperature. The value of P falls with increasing temperature. By development at 38° C the value of P is one—third lower than by development at 12° C. The P/D or $P/\log E$ curves have similar form as before. Maximas which appeared on the curves P/D or $P/\log E$ at 20° C for medium development times, were not apparent at 12° C. At development temperature of 28° C the number of "maximas" on curve P/D is greater than at 20° C—at 38° C, their number and height is reduced along with the lower value of the photometric equivalent.
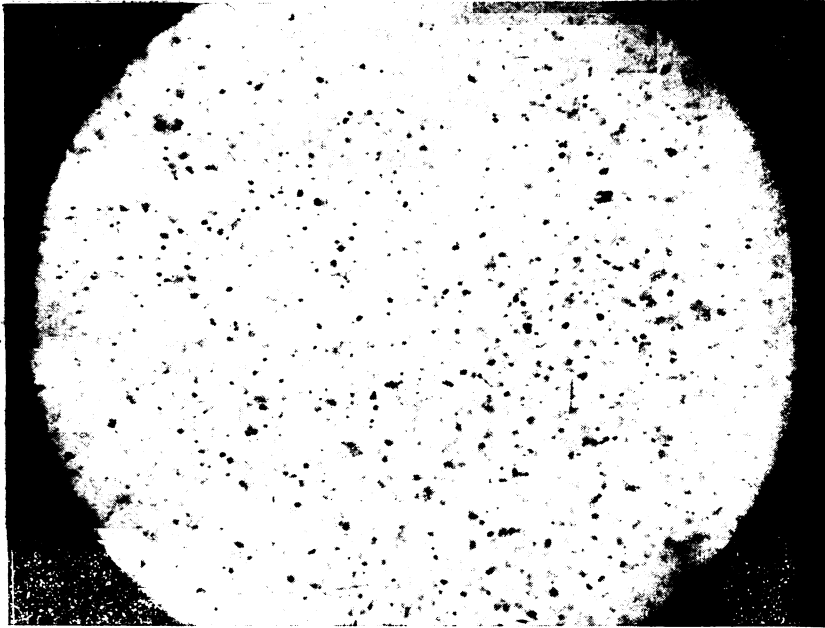
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Fig. 9. Microphotograph showing developed grains of fine-grained negative
material Agfa Isopan FF.
(D = 1.6, ferro-oxalate developer, t = 5 min.), Total magnification is 5400

The fall in the value of P with increasing temperature of development necessarily assumes a change in size or shape of developed grains and therefore in a change of the so called covering force (the covering force is called the reciprocal value of the photometric equivalent). Fig. 16 shows the mass of deposited silver that is necessary to give optical density $D = 1.5$ for different development temperatures. The same fig. shows, that at higher temperatures of development the amount of deposited silver needed to give a constant optical density is less than for lower temperatures.

The increase of the covering force can be explained by the enlargement of the total area of deposited silver. The relation between the concentration of reduced silver needed for a given optical density and development temperature is shown in fig. 17. From the demonstrated dependencies it follows that the covering force at development temperature of 38° C is about three times as large as at 12° C.

The presumption. that with changes in development temperatures, changes sn size and shape of grains (and therefore changes in the total area of deposited silver) occured is satisfied by microphotographs of developed silver grains. Fig. 18 and 19 show the shape and size of developed grains at 20 and 38° C. There is a marked difference between the shape and size of grains developed at 38° C and those developed at 20° C. The grains corresponding to 38° C are rod-ihaped whereas at 20° C they are spherical. The average size of grains is also
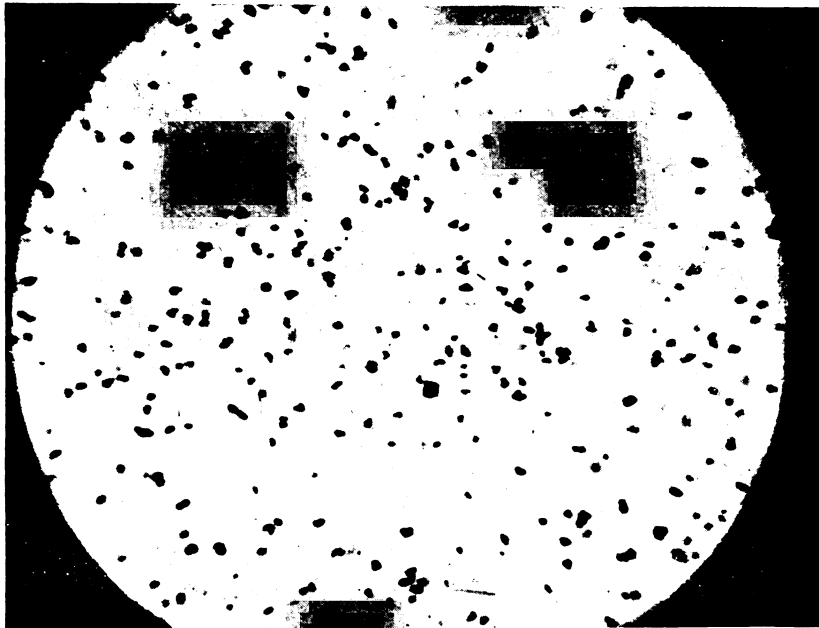
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Fig. 10. Microphotograph showing developed grains of material Agfa Tf 4.
(D = 1.95, ferro-oxalate developer, t = 8 min.).

smaller. The enlargement of the total grain area explains the lower values of
the photometric equivalent and higher covering force of silver agregates formed
at higher development temperatures.

A comparison of results obtained from the study of P/D with those found by Shepp-
ard and Ballard[2].

The results shown in fig. 21 are taken from the work published by SHEPPARD
and BALLARD. These results were compared with measurments of P/D discussed
in this paper. It was found that our dependences P/D differ from those obtained
by the cited authors specialy for Tf 4 materials. For Isopan FF materials the
results are comparable. The discrepancies for Tf 4 materials are probably caused
by different properties of the sensitive material i. e. different distribution of
grain size.
   It is interesting to note that although the authors used a colorimetric method
(which in our opinion is less reproducible than the potenciometric method) to
evaluate the analytic concentration of depositied silver they obtained values of
P which do not conform with the fact that P/D should be linear for low values
of D. The authors cite their results in tables but do not use them in the discuss-
ion of the variation of P/D. It is possible that they believed that the discrepan-
cies in the values of P were experimental errors. The "maximas" that appeared
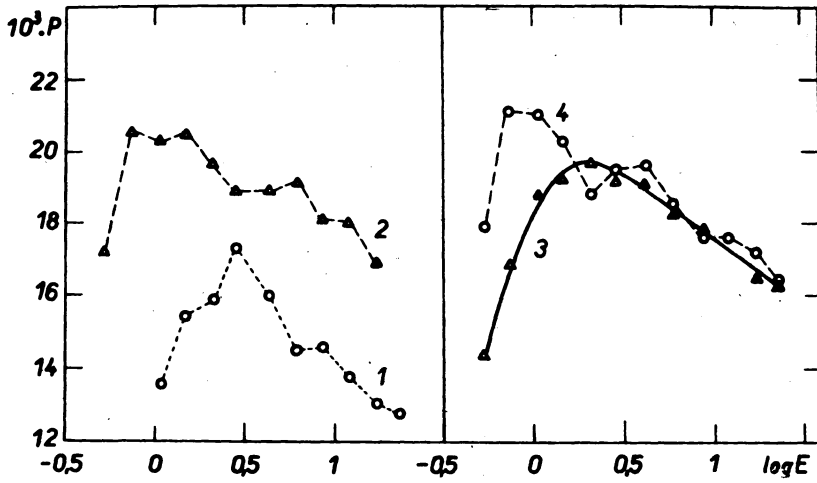on the P/D curves for short and medium development times (for Tf 4

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Fig. 11. A graph of P/log E for material Agfa Tf 4 developed
in an inorganic ferro-oxalate developer.
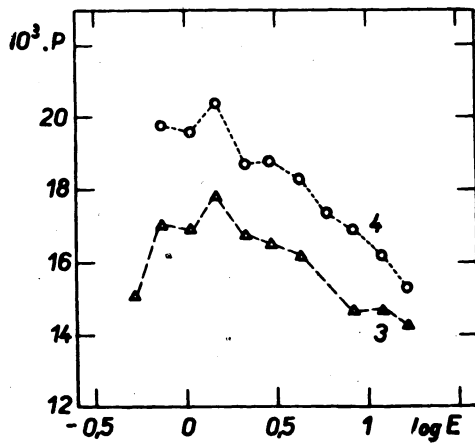Development times: 1—2 min., 2—8 min., 3—12 min., 4—20 min.

Fig. 12. Graph showing P/log E for Agfa
Tf 4 material developed in developers
with organic reducing agents.
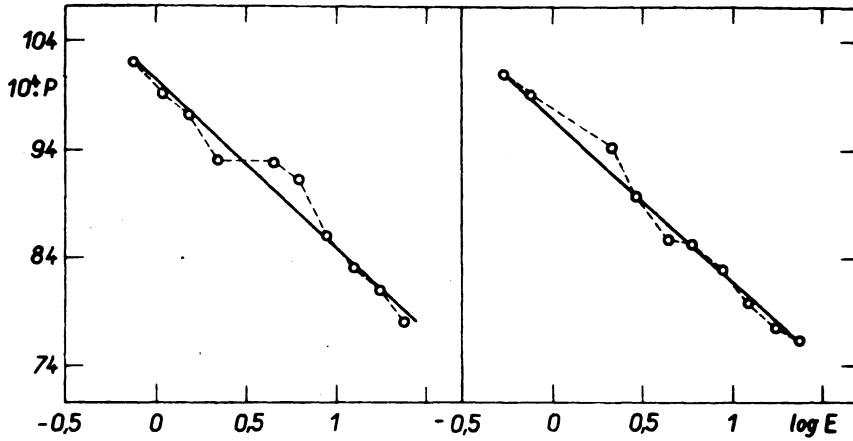Curve 1 - fenidone developer, curve 2 -
Kodak D 76 developer.

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Fig. 13. Graph showing P/log E for fine-grain negative material Agfa Isopan
FF developed in ionorganic ferro-oxalate developer.
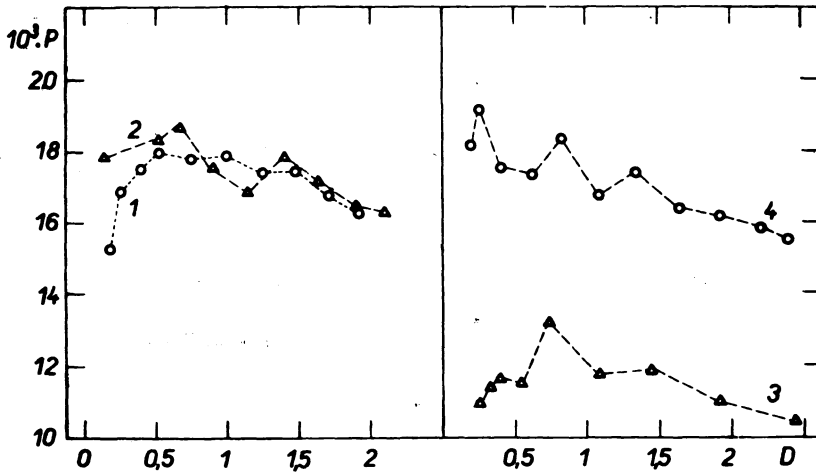Development times: curve 1 - 5 min., curve 2 - 10 min.

Fig. 14. Graph showing the relation P/D at different development
temperatures for material Agfa Tf 4.
Development temperatures: 1—12° C, 2—20° C, 3—28° C, 4—38° C.
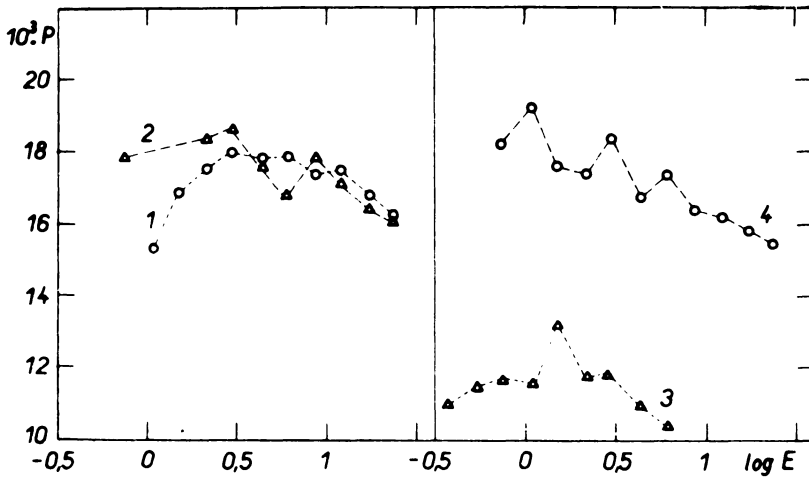Ferro-oxalate developer, development time 8 min.

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Fig. 15. Graph showing P log E at different development temperatures
for Agfa Tf 4 material.
Development temperatures: 1—12° C, 2—20° C, 3—28° C, 4—38° C.
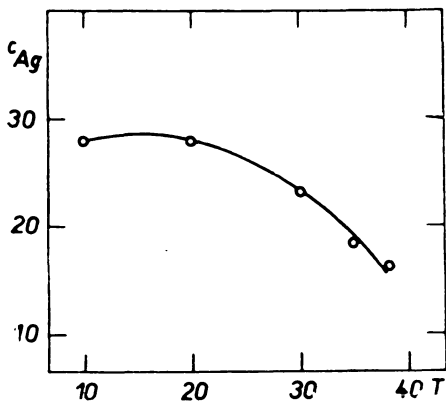Ferro-oxalate developer, development time 8 min.

Fig. 16. The relation between the
mass of deposited silver and develop-
ment temperature for optical density
D 1.5. (The mass of silver is given
in gms on area 10^5 sq. cm, temperat-
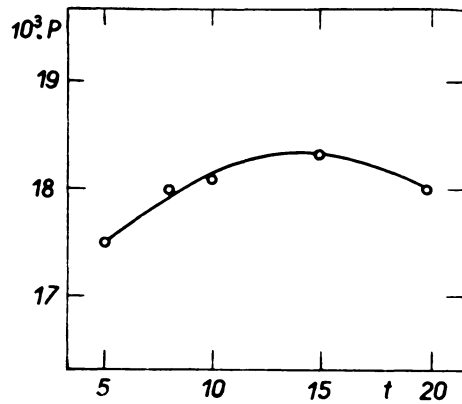ure is given in degrees centigrade).

Fig. 17. The relation between the
mass of deposited silver producing a
definite optical density and develop-
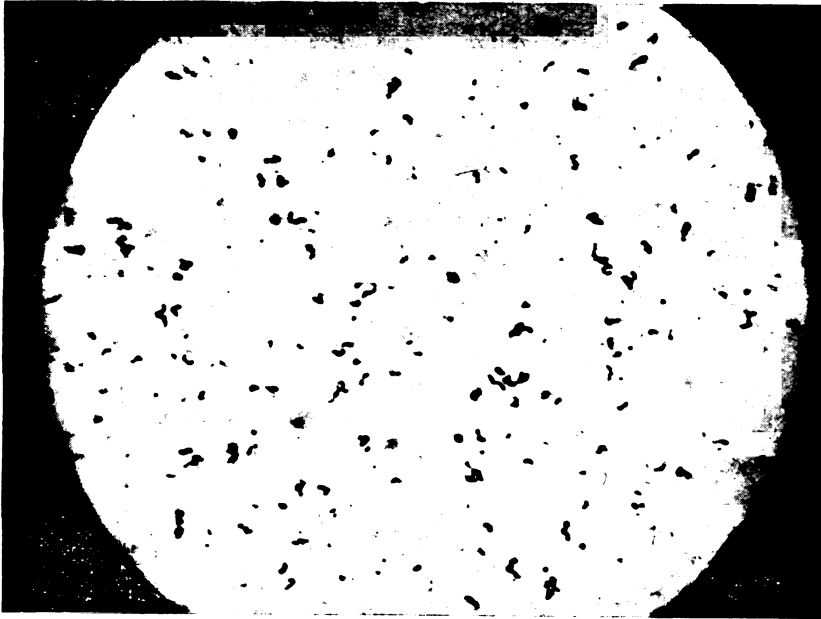ment temperatura. Curves: 1—12° C,
2—20° C, 3—35° C, 4—38° C.

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Fig. 18. Microphotograph showing grains of material Agfa Tf 4 developed in a ferro-oxalate developer at 38° C. (D = 1.95, t = 8 min.). Total magnification is 5400.
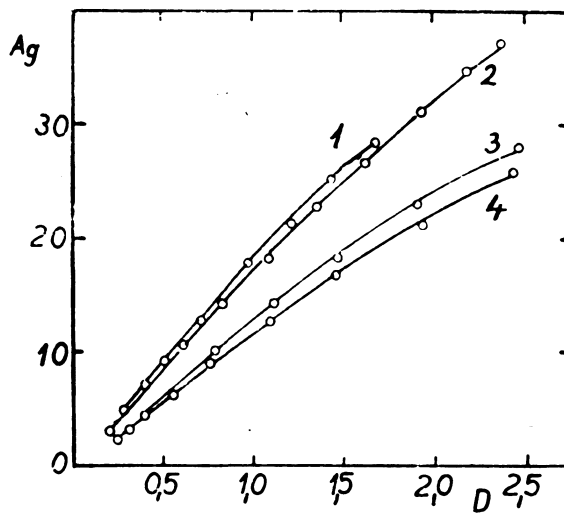

Fig. 20. The relation between the photometric equivalent and development time for Agfa Tf 4 material.
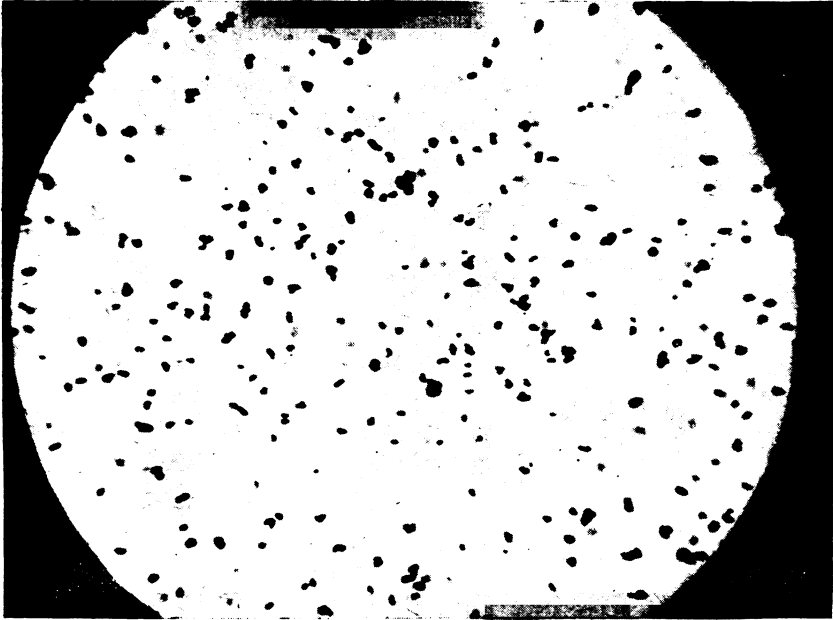(Ferro-oxalate developer, defined for D = 1.5).

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Fig. 19. Microphotograph showing grains of positive material Agfa Tf 4
developed in a ferro-oxalate developer at 20° C. (D = 1.95, t = 8 min.).
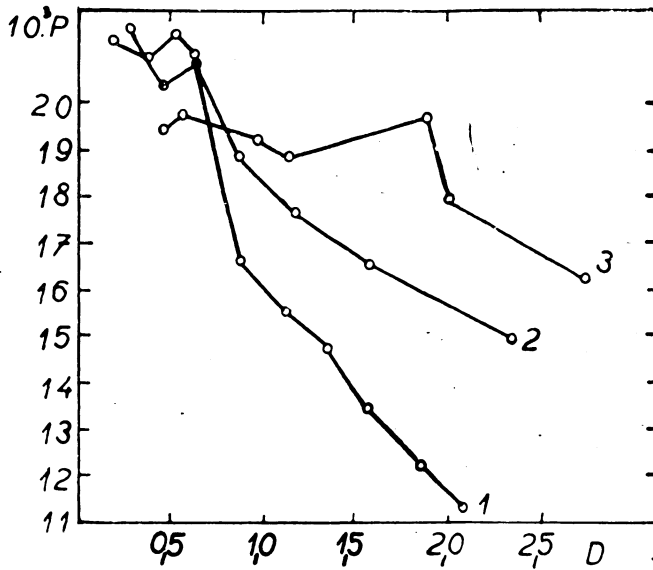Total magnification is 5400.

Fig. 21. A graph showing P/D obtained from data of
Sheppard and Ballard.
Curves: 1 - Special film, 2 - commercial film, 3 - East-
man 33 plates.

materials) are not taken into account by SHEPPARD and BALLARD. Further we have not found a mention of a rapid rise in P for very small values of D.

The dependence of the photometric equivalent on development time and type of applied developer.

If the dependence of the photometric equivalent on development time for an optical density lying on the linear part of the characteristic curve (fig. 20) is plotted, it is apparent that the value of P rises with increasing development time until it reaches a definite value. For still longer development times the value of P shows a slight decrease. A similar relation was found between the ratio of the concentration of oxidised products in ferro-oxalate developers to D and development time.

The dependence of P on type of applied developer or reducing agent was observed in all previous studies. It is natural because in the first place a molecule of the reducing agent itself influences the speed of development and secondly the chemical composition of developers is an important factor in the development of grains of defined size.

CONCLUSION

It was found that the dependence of P on D studied on Tf 4 material is rather different from that measured by SHEPPARD and BALLARD.

The study of the dependence of the photometric equivalent on optical density, logarithm of exposure, time and temperatures of development was carried out on two materials of greatly different properties. These measurements were supplemented by studies of size and shape of emulsion grains on an optical microscope. In order that a comparison of size and shape of grains of the used materials could be made, the grains were photographed by means of an electron microscope.

The determination of the mass of deposited silver for the study of the photometric equivalent was accomplished by a potenciometric method which is more reproducible then the colorimetric method.

ZÁVĚR

Bylo ukázáno, že průběh závislosti fotometrického ekvivalentu na optické hustotě, sledovaný u středně citlivého materiálu, vyráběného v současné době, se podstatně liší od průběhu téže závislosti sledované SHEPPARDEM a BALLARDEM.

Studium závislosti fotometrického ekvivalentu na optické hustotě, logaritmu exposice, době a teplotě vyvolávání bylo provedeno na dvou — vlastnostmi zcela odlišných materiálech a doplněno sledováním velikosti a tvaru vyvolaných emulsních zrn na optickém mikroskopu. Možnost porovnání velikosti a tvaru zrn u použitých citlivých materiálů byla dána provedením snímků emulsních zrn na elektronovém mikroskopu.

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Ke stanovení množství vyvolaného stříbra při studiu fotometrického ekvivalentu byla použita potenciometrická metoda, která zaručovala reprodukovatelnější výsledky, než používané metody kolorimetrické.

SOUHRN

Byla sledována závislost fotometrického ekvivalentu na optické hustotě, logaritmu exposice, době a teplotě vyvolávání a na druhu použité vývojky. Při studiu těchto závislostí bylo použito dvou zcela odlišných materiálů — nesensibilovaného materiálu Tf 4 s citlivostí 11/10 DIN a jemnozrnného materiálu o citlivosti 10/10 DIN. Studium závislosti fotometrického ekvivalentu bylo doplněno sledováním velikosti a tvaru vyvolaných emulsních zrn na optickém mikroskopu. Výsledky získané v této práci byly porovnány s výsledky práce SHEPPARDA a BALLARDA.

ЗАКЛЮЧЕНИЕ

Авторы выявили, что зависимост фотометрического эквивалента от оптической плотности, определяемая у выпускаемого в настоящее время материала Tf 4 в значительной степени отличается от этой же зависимости, установленной Шейпардом и Баллардом.

Определение зависимости фотометрического эквивалента от оптической плотности, логарифма выдержки, времени и температуры проявления проводилось на двух, по своим свойствам совершенно различных материалах и сопровождалось, кроме того, определением величины и формы проявленных эмульсионных зерн оптическим микроскопом. Возможность сравнивать величину и форму зерн на использованном чувствительном материале была дана съемкой эмульсионных зерн электронным микроскопом.

Для определения количества проявленного серебра при вычислении фотометрического эквивалента применялся, в отличие от работ Шейпарда и Балларда, потенциометрический метод, дававший гарантию получать более отчетливые результаты, чем те, которые дает колориметрический метод.

ВЫВОДЫ

Определялась зависимость фотометрического эквивалента от оптической плотности, логарифма выдержки, времени и температуры проявления и от вида использованного проявителя. При изучении этих отношений были использованы два совершенно разных материала — негативный материал TF4 со светочувствительностью 11/10 DIN и мелкозернистый материал Isopan FF со светочувствительностью 10/10 DIN.

Определение зависимости фотометрического эквивалента сопро-

вождалось, кроме того, определением величины и формы проявленных эмульсионных зерн оптическим микроскопом. Полученные в процессе этой работы результаты авторы сравнили с данными Шейпарда и Балларда.

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