Translations of Five Articles on Infrared from Zeitschrift für Physik

Translations by L. Tiffany and M. Tribus

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CONCERNING PHOTOGRAPHY IN THE INFRARED

M. Czerny, Zeitschrift für Physik, 53, 1, 1929

Translation by L. Tiffany

ABSTRACT

The methods formerly used for photography in the infrared are useful only to about two microns. It does not seem likely that it can be extended to longer wavelengths, since black body radiation at room temperature is so marked that the process will proceed without the image rays. The following new method is not limited by this difficulty. A thin white layer of napthalene is deposited on a celluloid membrane, and then put in an enclosure saturated with napthalene vapor. The infrared rays are changed by absorption into heat and serve to sublime the napthalene differentially from the irradiated and non-irradiated locations. The limits and possibilities of the method are considered and the results of experiments presented which show that the method is useful.

Since the discovery of the sensitization of the photographic plate by dyes, no method has been found to make the plates sensitive to longer wavelengths. It is possible to produce plates with which one can work in the neighborhood of one micron. These methods have a great practical value for the near infrared. If, however, one considers the fact that with known thermal instruments it is possible to work out to about 400 microns it can be seen that the fraction of the infrared spectrum in which photography can be used is negligible. Two other methods are coming into use. One uses the fact that a ZnS layer which has been excited to phosphorescence will emit the phosphorescent light in a shorter time if under the influence of infrared light than it would normally, so that after a time the places irradiated with infrared appear darker than the remaining part of the ZnS layer. With this method it is possible to work out to about 1.7 microns. The other method proceeds from the observation that the fogging which is produced in an ordinary photographic emulsion by a brief general illumination may be removed by a later irradiation with infrared. This method has proved useful to about 1.13 microns.

If one asks the question, whether these methods can be extended to longer wavelengths, it seems necessary to me to consider the following line of reasoning, aside from the fact that many fruitless experiments have been made. In black-body room-temperature radiation, which is typical of the laboratory, there are almost no quanta which are in the visible or near infrared. Equally few occur in the air or other material. If therefore a plate is sensitized for the visible or near infrared, then every quantum from this spectrum region is an unusual event (since it comes from a source at higher temperature) which it neatly records. It is different for the plate which is sensitized to four microns or even farther into the infrared. Four-micron quanta occur in great quantities in room-temperature black-body radiation, so that the photographic process will occur in the dark, before and during the exposure to the rays which it is desired to register. The plate would therefore not be usable, but would fog itself. The following numerical table (Table I) shows how quickly the boundary conditions change for a photographic process as we go into the infrared.

TABLE I

Wavelength (microns)	Black-body quanta	Equivalent distance	Number of molecules	Number of quanta in spectrum
≤ 1	$3.0 \cdot 10^{0}$	3330 km	$5.5 \cdot 10^{3}$	$0.4 \cdot 10^{16}$
1--1.5	$1.9 \cdot 10^{7}$	1.36 km	$5.8 \cdot 10^{10}$	$1.4 \cdot 10^{16}$
1.5--2	$4.0 \cdot 10^{10}$	29 m	$1.5 \cdot 10^{14}$	$1.5 \cdot 10^{16}$
2--2.5	$3.6 \cdot 10^{12}$	3 m	$1.6 \cdot 10^{15}$	$1.3 \cdot 10^{16}$
2.5--3	$7.0 \cdot 10^{13}$	71 cm	$3.7 \cdot 10^{17}$	$1.0 \cdot 10^{16}$
3--4	$2.4 \cdot 10^{15}$	12 cm	$1.7 \cdot 10^{19}$	$1.4 \cdot 10^{16}$

The second column of the table shows how many quanta contained in the spectral region given in the first column, from the black-body of the laboratory at T = 290°K, fall on each side of a surface of one square centimeter per second. The numbers are calculated from the following formulas:

$$E_\lambda \, d\lambda = 2\pi \cdot 2c^2 h \frac{\lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} d\lambda = h\frac{c}{\lambda} \, dn,$$

$$n = \int_{\lambda_1}^{\lambda_2} dn = 4\pi c \int_{\lambda_1}^{\lambda_2} \frac{\lambda^{-4}}{e^{\frac{c_2}{\lambda T}} - 1} \, d\lambda,$$

$$n = 4\pi c \, \frac{T^3}{c_2^3} \left[\frac{x_2^2 + 2x_2 + 2}{e^{x_2}} - \frac{x_1^2 + 2x_1 + 2}{e^{x_1}} \right],$$

$$x_1 = \frac{c_2}{\lambda_1 T}, \qquad x_2 = \frac{c_2}{\lambda_2 T}.$$

The formula in the first line tells how much energy, according to the Planck radiation law, falls in unpolarized rays on both sides of one square centimeter per second. The right half of the formula shows how this energy is divided between dn quanta of energy: $hr = h\frac{c}{\lambda}$. The formula of the second line gives the number n of quanta belonging to the

finite region of spectrum from λ_1 to λ_2. In the third line the integration is carried out, under the simplifying assumption that $\frac{c_2}{\lambda T}$ is very large compared to one, so that one can neglect -1 compared to $\frac{c_2}{e^{\lambda T}}$ in the Planck radiation law, and calculate with the Wien radiation law. This assumption is fulfilled in the case under consideration. The table shows how extraordinarily quickly the number of black-body quanta grows if one proceeds into the infrared, and how as a result the boundary conditions change basically for photographic processes.

In order to see the meaning of this more clearly, in column 3 we calculate the distance at which one must place a Nernst burner to give the same number of visible quanta per second per square centimeter as is given in column 2. For the calculation it is assumed that the Nernst burner radiates like a black-body of T = 2300°K and one-square-centimeter surface. As the visible spectrum region we take wavelengths from 0.4 to 0.7 microns or 4000 to 7000 Å. A photographic plate which is sensitized for this region and only for this region will fog in a short time, if the Nernst burner is placed at a distance of 30 m, therefore in a flux of the order of 10^{10} quanta per cm^2 per second.

These reflections are not complete since the important thing is not the absolute number of black-body quanta which fall in a spectral region but their ratio to the number of quanta which can be obtained from an artificial source in the same spectral region. Column 5 of the table will illustrate this. Assume a spectroscope is used with a slit 0.2 mm wide and one cm long, on which is focussed a black-body source at T = 2300°K (Nernst burner). The spectroscope has a mirror five cm in diameter and of 35 cm focal length. Let 50 per cent of the radiation be lost through reflection and absorption in the prism. The dispersion of the prism is such that the spectral region given in column 1 is concentrated in a band of one cm length. Under these conditions column 5 gives the number of quanta per second per square centimeter in each of the spectral regions. One sees that in the short wave infrared a significantly higher number of quanta may be obtained experimentally than in the visible, and that at about four microns the number of black-body room-temperature quanta becomes comparable to that obtained in the same spectral region from the Nernst burner.

Finally, in column 4 is given the number of air molecules (atmospheric pressure) which fall on one side of one square centimeter per second with kinetic energy equal to the energy of a quantum in the spectral region under consideration. If $1/2\ \mu v^2$ is the kinetic energy of a molecule, then we set

$$1/2\ \mu v^2 = h\nu = h\frac{c}{\lambda} \cdot$$

Such a molecule may generate a quantum of wavelength λ by a collision process. The number of molecules given in the table is calculated in the usual way from the Maxwell velocity distribution according to the following formula:

$$Z = \left(\frac{\mu}{2\pi kT}\right)^{3/2} n \int_{v_1}^{v_2} v^3\, e^{-\frac{\mu v^2}{2kT}}\, dv\ ,$$

$$Z = n\sqrt{\frac{kT}{2\pi\mu}}\left[\frac{1+y_1}{e^{y_1}} - \frac{1+y_2}{e^{y_2}}\right],$$

$$y_1 = \frac{\mu v_1^2}{2kT} = \frac{1}{kT}\cdot\frac{hc}{\lambda_1}\ ,$$

$$y_2 = \frac{\mu v_1^2}{2kT} = \frac{1}{kT}\cdot\frac{hc}{\lambda_2}$$

(n is the total number of molecules per cubic centimeter).

The table shows that about ten times as many molecules strike the surface as quanta of the same energy content. One would obtain similar

numbers if one asked how many molecules of a solid had the given energy content.

The above considerations indicate that it is impossible to develop ordinary photography or any method equivalent to it for wavelengths longer than about two or at most four microns because of the dark-reaction which will hinder or completely obscure the desired photographic recording.

In what follows a sort of photographic process will be described which also is affected by this dark reaction, but in which it remains unnoticeable. Therefore this process can be used for photographic recording to arbitrarily long wavelengths. If one spreads a solid material which has a noticeable vapor pressure at room temperature, such as camphor or napthalene, in a very thin layer and puts the whole in an enclosure which is saturated with the vapor of the substance, then rays from outside which are absorbed in the substance warm the substance where they fall. The material sublimes from these locations and recondenses on locations which were not irradiated. The irradiated places then become thinner, thus showing that radiation fell there. If the radiation is interrupted the spot returns to room temperature and does not become thinner. The substance in equilibrium with its vapor forms a stationary state, in which as many molecules evaporate from a spot as recondense. This process is the dark reaction which does not influence the sublimation due to irradiation.

The practical execution can be accomplished in the following way: A glass tube of about 15 cm length and 5 cm diameter is closed at one end by a celluloid membrane of about 0.5 microns thickness. The membrane is covered on the outside by a layer of soot.[1] The other end of the tube is closed by a tightly fitting cork. About in the middle of the tube is placed a small glass tube, closed at one end, wrapped with a heating wire. An electric current is passed through this coil from electrodes which pass through the cork. Camphor, napthalene, or a similar material is placed in the small glass tube, and the entire apparatus is mounted vertically, so that the membrane is below (compare Figure 1). Now the small tube with the camphor is heated. The camphor

[1]Compare Zeits. f. Phys. 34, 231, 1925.

melts, boils, and forms a camphor fog which is deposited everywhere, including on the membrane. When the layer is thick enough to form a thin uniform white layer which extinguishes the interference colors of the membrane, the evaporation is stopped and the layer is ready. If radiation is allowed to fall on the smoked side of the membrane, the soot layer will be warmed at this place, the heat will be conducted through the membrane to the camphor layer, and the camphor will begin to sublime. Such a layer is sensitive to every kind of ray which the soot will absorb.[1]

If one omits the layer of soot and throws a continuous spectrum on the membrane, the camphor vaporizes only on the spots which are irradiated with waves which it strongly absorbs. One thus obtains the absorption spectrum of the camphor or similar material which was deposited on the membrane. This second experiment shows an important difference from the one using soot absorption. If the absorption takes place in the soot, large intensity differences in the radiation cause a difficulty, for on a strongly irradiated spot the entire layer can sublime, before there is anything noticeable at a weakly irradiated spot. If the camphor itself is the absorbing medium, then, although the strongly irradiated spots sublime more quickly at first, as the camphor layer becomes thinner its absorption decreases, and theoretically it requires an infinite time to sublime all the material at a given spot. Indeed in the practical application of the method it can be seen that the experiment goes more easily, that greater differences in intensity can be shown.

The value of the method depends on subliming from irradiated to non-irradiated spots as quickly as possible. It is therefore necessary to choose substances which at room temperature have as high a saturation pressure as possible, perhaps camphor ($p = 0.50$ mm) or napthalene ($p = 0.054$ mm). As will be calculated later, camphor works more quickly than napthalene. The ratio will be different however, if the sublimation is carried out at the lowest possible gas pressure, rather than

[1]As a precursor of these experiments, a method should be mentioned which was given by Herschel in 1840. He soaked filter paper in alcohol. An irradiated spot on the paper then dried more quickly than did the background. The essential difference between that method and this is that he did not carry out the experiment in an atmosphere of alcohol vapor.

atmospheric pressure. As is known, in determining the speed of sublimation it is important to know how quickly the vapor molecules can diffuse. The diffusion velocity increases quickly if the gas pressure is lowered, and only reaches a limit when the mean free path is of the order of magnitude of the dimensions of the container, that is at a pressure of the order of 0.001 mm Hg. However, the gas pressure can be lowered only to the saturated vapor pressure of the substance. Thus with camphor one can work only to about 1 mm, with napthalene to about 0.1 mm. At these smallest usable pressures, the sublimation goes as quickly with napthalene as with camphor. As a result of the evacuation, the sublimation velocity of camphor is increased by a factor of less than 100, while that of napthalene is increased by a factor of about 1000. Under these conditions the napthalene layer is to be preferred to the camphor layer because it may be desensitized to the radiation by admitting air at atmospheric pressure. In working with substances whose saturation pressure lies appreciably under that of napthalene, a limit is reached where the diffusion cannot be appreciably increased, and the less strong sublimation process can no longer be compensated.

In order to sublime the thickest possible layer with a given quantity of energy, the substance must have the lowest possible heat of sublimation. The sublimation heats of the substances considered are of the order of 100 cal/g. With this value it may be easily calculated what can be expected in the most favorable case, if radiation measurements were made with the help of such a sublimation process. If a Hefner candle is placed one meter from the preparation, then it is known that 7.7×10^{-2} cal/hr fall on each square centimeter of the preparation. If ℓ is the sublimation heat per gram and σ the density, then one calorie can sublime $1/\ell$ grams or $\frac{1}{\ell\sigma}$ cm^3. If we make the assumption that the heat of the candle is used for sublimation without loss, then under the action of these rays $\frac{7.3 \quad 10^{-2}}{\ell\sigma} cm^3$ sublime per hour. If one sets ℓ -100 cal/g and σ = 1, we obtain 7.7×10^{-4} or 7.7 μ. This is not a very strong effect. Thus it can only be expected that very small changes in layer thickness can be obtained.

These numbers are obtained under the simplifying assumption that all radiation is used for sublimation, and none lost through heat conduction,

radiation or the like. The experimental results with napthalene under a vacuum of about 0.1 mm imply that this simplifying assumption is approximated. This is also clear from the following consideration: let the molecular weight of the subliming substance be M, the room temperature T (^{o}K). Over the substance will be found only its vapor, whose saturation pressure p is of order 0.01 mm Hg. Sufficient heat is added to a small surface element of the substance to warm it to T + ΔT. The quantity of heat may be divided into one part which is used to supply the heat of sublimation (this is the useful part) and another part which supplies the loss of heat through radiation and conduction. The first part may be calculated in the following way: from known formulas of gas theory one can determine how many vapor molecules fall per second on one square centimeter of the substance. The mass G_T of this quantity of molecules is

$$G_T = 5.84 \times 10^{-2} \sqrt{M} \quad \frac{p}{\sqrt{T}}$$

Under the assumption that all molecules which strike the surface remain and that the same number re-evaporate in the steady state, G_T is also the number of grams which evaporate per second per square centimeter. If now a particular square centimeter of substance is heated to ΔT over room temperature, then per second there sublimes from this square centimeter

$$G_{T + \Delta T} - G_T = 5.84 \times 10^{-2} \sqrt{M} \quad \frac{\partial}{\partial T} \left(\frac{p}{\sqrt{T}}\right) \quad \Delta T$$

and if ℓ is the sublimation heat per gram, the quantity of heat necessary for the sublimation is

$$Q = \ell \left(G_{T + \Delta T} - G_T\right) = 5.84 \times 10^{-2} \ell \sqrt{M} \quad \frac{\partial}{\partial T}\left(\frac{p}{\sqrt{T}}\right) \quad \Delta T$$

Here the assumption is made that the saturation pressure of the substance is very low, and the mean free path of the molecules sufficiently large that the molecules which strike can be described by the temperature T, while the surface element under consideration has a temperature T + ΔT. For napthalene ℓ = 100 cal/g, M = 128, p = 0.054 mm for T = 293, and p = 0.035 mm for T = 288. Therefore

$$\frac{\partial}{\partial T}\left(\frac{p}{\sqrt{T}}\right) = 2.2 \times 10^{-4}$$

and $Q = 1.45 \times 10^{-2}\ \Delta T$ cal/cm^2 sec. This quantity of heat must therefore be added per cm^2 sec to supply the heat of sublimation. On the other hand the quantity of heat which is necessary to supply the radiation loss can be calculated under the assumption that the layer radiates like a black body at a temperature $290 + \Delta T$, following the Stefan-Boltzmann law. This amounts to $Q = 1.34 \times 10^{-4}$ cal/cm^2 sec.[1] This quantity of heat is therefore 100 times less than that necessary for sublimation. The remaining heat loss through conduction in the thin layer and the neighboring gas is also of the order of magnitude of the radiation loss. This can be confirmed by an approximate calculation or by drawing upon the known results concerning the increase in sensitivity of surface thermoelements when brought into a vacuum. It follows that of the quantity of heat which must be introduced, in order to hold a surface element ΔT above the temperature of the surroundings, the greatest part is used to supply the heat of sublimation. The sublimation process thus proceeds with good efficiency.

The experiments conducted thus far have been of a rather provisional, orienting character. As already mentioned several times, they have been done with camphor and napthalene. Attempts to use anthracene were unsuccessful, since the vapor pressure of this material is too low. Figures 2 and 3 show photographs of napthalene layers on which a continuous infrared spectrum was thrown.[2] Napthalene was sublimed from those spots where it was illuminated by rays which it strongly absorbs. As the figures show, these spots are clearly black, when one places a black paper behind the layer and illuminates from the front. The spectrum in Figure 2 was obtained with 20 minutes infrared exposure and shows four absorption lines in the region from about 1.5 to 3.5 μ. The second exposure was 90 minutes long, so that the short wavelength part is overexposed. However, long wave absorption lines are clearly shown, especially one at about 6 μ.[3] During the exposure the layer was kept in a glass tube which was pumped to about 0.2 mm. Moreover, some P_2O_5

[1] Translator's note: ΔT was omitted here.

[2] The exposures were made with a camera on photomechanical plates. The pictures are positives.

[3] These exposure times may be reduced several times by the use of two plane mirrors in front of the layer so that the vertical extent of the line is concentrated in a smaller region.

was placed in the tube as a drier. In order to allow the infrared rays to enter the tube unhindered, it was closed with a large rock salt window. A Nernst pencil served as source, and was focussed on the slit of a mirror spectrometer. The instrument had a concave mirror of 5 cm diameter and 35 cm focal length. The second slit was removed and the napthalene layer put in its place. The prism was a 54^{o} fluorspar prism with a 4 × 5 cm side surface.

Of the other experiments which use soot as absorption material and use the sublimation layer only as an indicator, only investigations concerning the attainable sensitivity have thus far been made. In the use of a napthalene layer under about 0.1 mm pressure, the results obtained thus far can be described as follows: if the rays of a Hefner candle at one meter distance fall through a diaphram of about 1 cm diameter onto the layer, then in about 30 minutes the irradiated patch can be clearly distinguished from the surroundings. For many purposes this sensitivity is perhaps good enough; however, more sensitive radiation measuring instruments, I am sorry to say, are still necessary. For comparison consider the sensitivity of a Rubens microradiometer. Such an instrument gives a deflection of about 700 cm on a scale placed 5 meters away, when used with a Hefner candle at one meter distance. One must remember, however, that the cone of the instrument magnifies the deflection about fourteenfold; thus without the cone it would give a displacement of about 50 cm. A good thermopile in air with thirty elements, together with a medium sensitivity galvanometer gives about seven cm deflection with five meters scale distance and one meter distance of the Hefner candle. The results which have been obtained seem sufficiently promising to attempt to extend the method. The number of possible variations in the choice of the absorbing layer, the base material, the subliming layer, the method of making thinned spots visible, etc., is very great and permits the hope of important improvements.

I owe great thanks to Dr. Schmerwitz and Cand, Phys. Wurbs for helping me with the experiments.

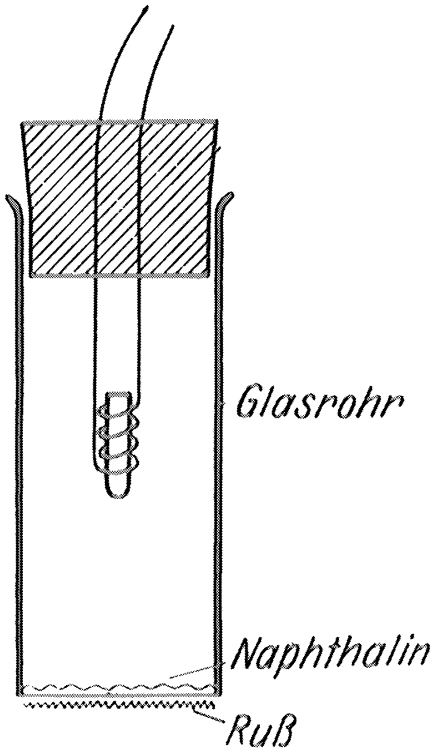

Figure 1

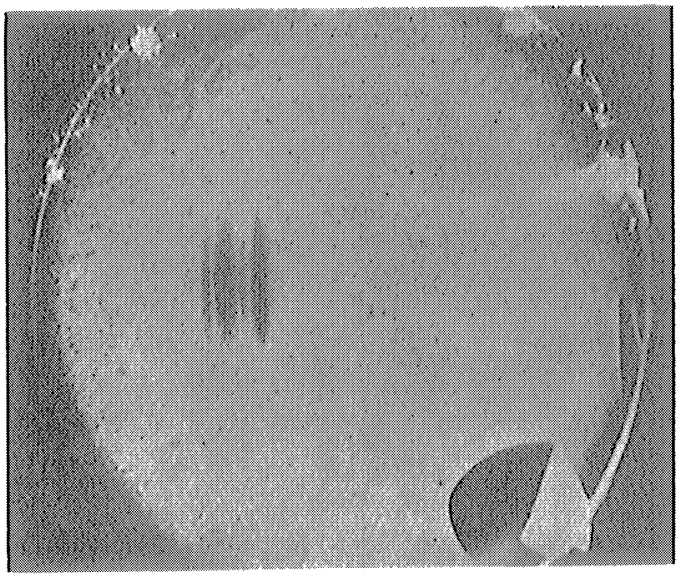

Figure 2

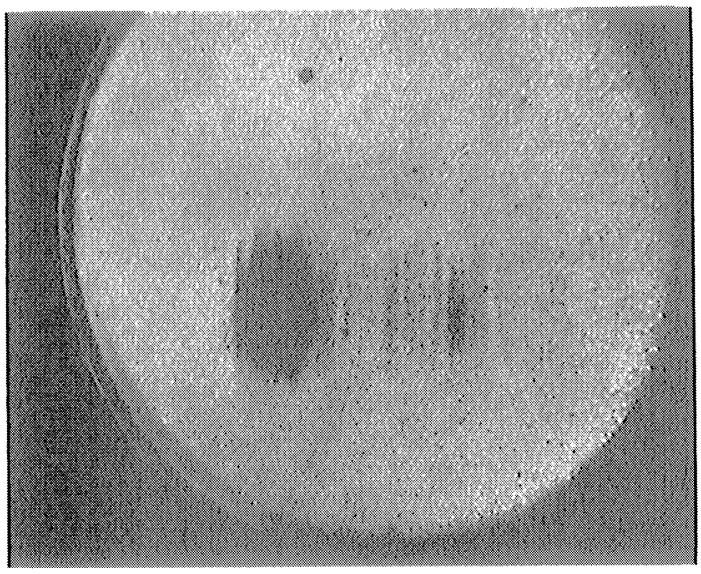

Figure 3

INFRARED PHOTOGRAPHY

Herman Willenberg, Zeitschrift für Physik, 74, 663, 1932

Translation by L. Tiffany

ABSTRACT

The method of photography in the infrared proposed by M. Czerny is developed further. The incoming energy is used for evaporation of a liquid (oil) which is placed in a very thin layer giving interference colors on a similarly thin substrate which absorbs infrared (blackened zapon-lacquer membrane). With irradiation one can then detect very small changes in thickness of the fluid layer by the change in its interference colors and also measure the changes in thickness. The sensitivity of this method and the sharpness of indication of the method are satisfactory. On the other hand, longer exposures cannot be accomplished at present. Several spectra and a few infrared photographs are shown.

Some time ago M. Czerny[1] showed that infrared photography with sensitized photographic plates is limited through a kind of "dark reaction" and described a completely different photographic method which compensates for this dark reaction: The energy of the radiation is used to evaporate a heavy volatile substance which is spread in a very thin layer on a thin zapon-lacquer membrane, the back of which is blackened with soot. This membrane, which extends across a glass tube, is placed in a closed evacuated vessel which is saturated with the vapor of the volatile substance and which is provided with a window transparent to infrared. The first experiments were carried out with napthalene, among other materials, and showed the feasibility of the method. It was also pointed out in that work that the method could be refined in several ways. In the following the advances achieved in the intervening time will be described.

[1]M. Czerny, Zeits, f. Phys., 53, 1-12, 1929.

1. First a few words concerning the choice of the evaporating substance and the different possibilities of detecting small changes in thickness in thin layers.

Solid crystalline material may be easily recognized as a thin dull deposit and is in this way very suitable (thus, for example, napthalene). It is true that this type of layer tends to recrystallize. The smaller crystals have a higher vapor pressure and recrystallize "onto the larger". Thus the layer in general is granular and unsuitable for exact work.

This recrystallization has another effect: If a heat ray is focussed on a particularly fine-grained layer, the contrast resulting will increase after shutting off the radiation, because the crystals in the irradiated part are on the average smaller than those in the non-irradiated region, and therefore have a slightly higher vapor pressure. This effect was indeed noticed in fine-grained napthalene layers and represents in principle a form of developing process. Its exploitation appeared enticing at first glance, but would not be practical because at the same time the entire layer becomes unequally dense. An initially fine-grained crystal layer, which was subsequently intensified by very small systematic contrast, would also naturally increase in accidental contrast at the same time, so that an improvement of the picture by means of a developing process cannot be obtained. The gain in the photographic process is due to the fact that normally no random fog exists in the latent image.

Since these dull crystal powder layers can only be used for coarse work, it appears suitable to consider coherent clear crystal layers or glassy deposits. Here at the same time very sensitive optical methods of detection can be used. As an example, vacuum sublimation has been tried to cover the zapon-lacquer membrane with a clear napthalene layer. The napthalene vapor, however, only settled out on the walls of the chamber. Probably the membrane must be strongly cooled during the vacuum evaporation, which is technically difficult.

Since these and similar experiments with solids failed, further interest centered on liquids. Here too one works with vacuum evaporation. In general two groups of liquids could be distinguished: the one forms a dull deposit composed of very fine droplets on the membrane, just as in the case of the crystal powder deposit. The other adheres

completely to the substrate and forms a coherent layer with an even surface. (In the case of the thicknesses necessary here, namely a few tens of microns, the inner friction suffices empirically to prevent a disturbing flow of the layer; see below.) Here small changes in thickness may be detected well optically. The substrate has a dull surface as a result of microscopically small irregularities; then these irregularities are filled by the liquid and the surface is clear. On an irradiated spot it again becomes dull. This means of detection is very sensitive. As a result of the roughness of the substrate the vapor pressure of the liquid layer depends on the thickness of the layer (due to different curvature of the surface elements) so that the equilibrium between the liquid and its vapor is not completely independent.

On the other hand, if the substrate is clear, the thin fluid layer and its small changes in thickness may be easily detected and measured by the interference colors[1] which occur. This method has been investigated most and seems to be the most promising. If the index of refraction of the liquid used is not too different from that of the substrate, then both layers are seen as an optical unit. One then observes in reflected light the colors which result through interference of the wave reflected on the front side of the fluid layer f (Fig. 1) with that reflected on the back of the membrane m (r is the infrared-absorbing soot layer).

In order to obtain strong interference colors, one attempts to use substances of high index of refraction and above all to produce interference of lowest order (first or second) since with increasing order of interference the white light content of the interference colors greatly increases. One must therefore take care that the path difference g of the two interfering waves is less than 3λ (λ = mean wavelength of the viewing light, therefore $\lambda \sim 0.6\ \mu$).

The light path w through the layer m + f increased by $\lambda/2$ (the phase change of the wave reflected from the front of f) must therefore be as much less than 3λ as possible. The expression for the single light path $\frac{w}{2}$ through a thin layer of thickness m + f is

$$\frac{w}{2} = (m + f) \cdot \sqrt{n^2 - \sin^2 \alpha},$$

[2]Intense dyes of sufficient fluidity do not give these.

n = index of refraction ~ 1.5, α = angle of incidence. One then obtains the relation

$$g = w + \frac{\lambda}{2} = 2\,(m + f)\cdot\sqrt{n^2 - \sin^2\alpha} + \frac{\lambda}{2} < 3\lambda,$$

or for the case of normal incidence

$$m + f < \frac{5\lambda}{4n} = \frac{3\mu}{4n} = 0.5\,\mu\ .$$

This relation can be fulfilled practically, since zapon-lacquer membranes of $0.05\,\mu$ thickness have sufficient strength.

It is known that in the color scale of thin layers, a few colors are particularly easy to discern: for example if the thickness $m + f$ has the value $\frac{0.564}{n}\mu$ or $\frac{0.287}{n}\mu$, the eye will observe clear color contrast with small thickness changes (0.01 to $0.005\,\mu$!), as a glance at a table of colors of thin air layers shows[1] (for example, B. Kohlrausch, Lehrbuch d. prakt. Phys., older editions).

TABLE 1

Thickness in μ (n = 1)	Color
0.275	Deep red
0.282	Purple
0.287	Violet
0.294	Indigo
'	'
'	'
'	'

(Continued)

[1]In contrast to this is the consideration that these critical color tones take in appreciably smaller surfaces on the membrane in cross-section than the other colors.

TABLE 1 (Continued)

Thickness in μ (n = 1)	Color
0.550	Dark violet red
0.564	Violet
0.575	Indigo

These places are thus useful "working points", always remembering that this is only for visual observation. Before beginning an irradiation one therefore wets the membrane with the liquid to such a critical thickness m + f.

With the help of these especially easily distinguished interference colors the observation of adsorbed layers is also successful: a few liquids deposit in very thin layers on the membrane from the vapor phase. These can be noticed only if the membrane has such a critical color, at least in a few spots. A rough estimate of the observed color layers gives then for these fluid layers a thickness of about 0.001 to 0.006 μ, and therefore on each side of the membrane (naturally not smoked) about 5 to 30 Å. These are therefore adsorbed layers with very low vapor pressure.

For the purpose of infrared photography it is necessary that the fluid flow as little as possible on the substrate so that differences in layer thickness are not noticeably made even.

The velocity $\bar{v}$ with which a liquid layer of thickness ~ 0.1 μ flows down a vertical membrane as a result of its own weight is very small. Even in an unfavorable case with very low viscosity η, as for example petroleum ($\eta = 0.02$ cgs), the calculation gives only

$$\bar{v} = 1.3 \times 10^{-6} \text{ cm/sec.}$$

This low velocity causes no disturbance. On the other hand one could work with a horizontal membrane.

It is unacceptable under conditions where leveling of the differences in layer thickness occurs due to surface tension, as the following example shows: if a spectrum of barely resolved, nearly equidistant lines (for example a rotation-vibration band) falls on the membrane, then after a little time the thickness h of the fluid layer along the frequency scale (x direction) varies approximately sinusoidally between a maximum value $h = \bar{h} + A$ and a minimum $h = \bar{h} - A$ (h is then the mean thickness, A the amplitude of the variation). After the irradiation the surface curvature so produced is gradually lost through the capillary curvature pressure $p = \frac{a}{\rho}$ (a = constant of capillarity, ρ = radius of curvature of the surface). The amplitude A therefore decreases with time. This tendency toward equilibrium can be calculated. Knowing ρ one also knows the pressure gradient $\frac{\partial \rho}{\partial x}$; from this can be obtained the velocity of flow of the substance, and from this the rate of leveling -dA/dt. The calculation gives:

$$A = f(t) = A_o \cdot e^{-\frac{\pi^4 a \bar{h}^3}{3\eta \ell^4} t} = A_o \cdot e^{-\beta t},$$

and therefore a "half-life"

$$\tau = \frac{\ell n\, 2}{\beta} = \frac{\ell n\, 2 \cdot 3\eta \ell^4}{\pi^4 a \bar{h}^3} \text{ sec.}$$

(where ℓ is the wavelength of the sine curve).

As a numerical example I will choose the saturated hydrocarbon tridecane, $C_{13} H_{28}$, which is a very desirable working material for other reasons discussed further below. Then approximately:

$$\eta = 0.02 \text{ cm}^{-1} \text{ g sec}^{-1},$$

$$a = 26 \text{ g sec}^{-2}$$

Further let

$$\ell = 0.1 \text{ mm} = 10^{-2} \text{ cm},$$

$$\bar{h} = 0.05 \text{ mm} = 5 \times 10^{-6} \text{ cm},$$

then $$\tau = \frac{0.694 \cdot 3 \cdot 2 \cdot 10^{-2} \cdot 10^{-8}}{97 \cdot 26 \cdot 1.25 \cdot 10^{-16}} \text{ sec} = 1.38 \cdot 10^{3} \text{ sec.}$$

Therefore a sinusoidal liquid surface of the type considered here will be reduced to half-amplitude in $\tau = 23$ minutes by the curvature pressure. This effect has great influence in taking line-rich spectra under certain conditions. It must be considered in the choice of dispersion and slit width (further concerning this below). The dispersion corresponds to the factor ℓ (2ℓ is the distance between two "lines"), and therefore enters as the fourth power! The effect of the mean thickness $\bar{h}$ is almost as great. It should be kept as low as possible. The value of a/η varies rapidly and in general is much more satisfactory than in the example chosen. For example, with glycerine one obtains $a/\eta = \frac{66}{10.7}$ and thus $\tau = 77$ hours!

Among these disturbances peculiar to liquids another is to be noted. In the case of a vertical membrane the barometric change of the vapor pressure with height has an influence. At a pressure of ~ 0.05 mm Hg a change may be calculated; $\Delta h = 3 \times 10^{-8}$ cm/sec cm difference in height. This is clear after about 3 minutes when observing a strong contrast with Na light. In the case of the petroleum fractions used this effect is first noticeable at about 15 minutes and after this time can no longer be exactly measured.

The decrement can be sufficiently compensated, moreover, by a rather unequal deposition or by horizontal placement of the membrane and a corresponding bending of the path of the rays.

Investigations of the purely statistical variations in layer thickness have not yet been made.

The most easily obtainable and also otherwise suitable liquids are of limited chemical purity or are even complicated mixtures. The following difficulty then arises. In producing a thin layer (for example from petroleum or light oil) by evaporation in vacuum, the more volatile components of the mixture evaporate from the warmed container more than the less volatile. The thin layer resulting has a somewhat higher vapor pressure than the material in the container and thus will slowly

distill back; that is, the layer has only a finite lifetime. This difference in vapor pressure may be somewhat reduced by several distillations, by which in general the less volatile components of the mixture are enriched on the membrane; but the finite lifetime has meant an unpleasant hindrance in previous experiments. It is natural to try to lower the vapor pressure of the layer somehow, so that it is equal to that of the container. For example this might be accomplished by first bringing an extremely small quantity of a very slightly volatile oil onto the zapon-lacquer membrane. A membrane covered in this manner does not need to be evaporated on in the chamber, for it absorbs on itself a layer on the membrane from the vapor of the oil container. The vapor is absorbed strongly in the slightly volatile "vaccine" until an equilibrium concentration is reached. This sort of layer does indeed last almost indefinitely, but is also very insensitive. Moreover the pictures taken with them show an unnatural intensification of the edges of bodies. Figure 2 is reproduced as an "infrared shadow picture" of the small swallow-tailed notched metal strip shown again in Figure 16. Figure 2 does not give the impression of such a surface as the shadow-caster, but rather that of a wire figure of the same shape. (The wire pointing downward in the picture is part of the apparatus.)

Moreover, all mixtures have a further property. Under the assumption that the law of vapor pressure of mixtures depending on their mixture ratio is completely valid for such small quantities, the following is to be noted.

Assume it is possible to produce a thin layer of exactly the same composition as that of the material in the container. Its amount is small compared to that of the container. Then this layer does not have a finite life-time since its vapor pressure is the same as that of the material in the container. However this equilibrium of the layer with the vapor is not completely independent as in the case of a chemically pure substance. The vapor pressure varies with the layer thickness, especially during irradiation with infrared. It falls at the irradiated spots as a result of the preferential evaporation of the more volatile components. This results (in addition to a steadily lowering efficiency, see below) after interruption of the radiation in an increased condensation until equilibrium with the vapor is re-established. Thus the greater part of the change in thickness produced with the irradiation is lost.

On the other hand one can use large differences in intensity with appropriate combinations of such mixtures, for then the efficiency of the process soon sinks at the strongly irradiated spots as a result of local reduction in vapor pressure and finally practically nothing more evaporates. This sort of mixture is therefore used "soft".

2. The Experiments

Metal chambers with removable front windows were chiefly used as vacuum containers. Figure 3 shows one such container, in section.

The brass cylinder Z is closed on the left by a round metal plate P with a square window section in which is cemented a NaCl window S (50×50.9 mm^2). R is a ring which carries a protective cap K. The right side of the brass cylinder is closed by a glass observation window B. The G's are rubber seals. A connection with stopcock and resistance manometer W leads to the pump. A two-stage mercury pump is used for evacuation. The vacuum of 1/100 to 1/20 mm Hg which is produced is held very well by the rubber seals. The membrane M to be irradiated is placed on a brass ring (diameter 40 mm) which is screwed in with a small mount which is not shown. In use, the ring is coated very strongly with oil, as are all the metal surfaces. One must therefore not completely smoke the membrane to the edge, or the oil which is standing on the ring will penetrate the soot by capillary action and ruin it. The thickness of the soot layer is usually so chosen that it is practically opaque. Only brightly lighted bodies, as perhaps the coil of an incandescent lamp, can be seen clearly. Next to the membrane is found a small heating coil H, which is moistened with the liquid to be used. Finally by strong heating the spiral evaporates onto the membrane.[1] Then the spiral is turned to one side by its rotatable carrier T, so that one can observe the membrane during irradiation and also photograph it. These photographs are taken with an ordinary photographic camera with suitable plate and filter combinations (Filter: Schott colorglass GG11, 2 mm, or BG3, 1 mm. Plates: Agfa contrast plates and Perutz silver-eosin plates). For illumination a 200-watt lamp was used, whose heat

[1]One can also produce a liquid layer on a membrane without this introduction of heat: it is cooled evenly by bringing it into radiative contact with a cold body (liquid air or solid CO_2). A few preliminary experiments indicate that this method is useful.

radiation was removed by a water-filled condenser and a Schott glass BG9, 3mm. In order that the light from the viewing lamp not be reflected directly into the camera from the window B, the membrane M must be somewhat inclined to the plane of B. When the photograph has been taken, the oil residue can be removed by a short, general illumination, for example with an incandescent lamp. One can then begin again with a new evaporation and exposure, without admitting air. Thus one can often work with the same vacuum for an entire day. With a carefully prepared membrane very many exposures can be made, before it is spoiled (through loss of the soot layer, etc.).

The choice of a suitable fluid for production of the layer was difficult, for there are several properties to satisfy at the same time: the substance must be chemically pure for the reasons numbered above; moreover as inert as possible, when it touches the zapon-lacquer membrane[1] or other parts of the apparatus (metal parts, gasket, seals, Na Cl window).

In addition to this, for good pictures only materials can be considered which form coherent layers with interference colors, and which therefore completely wet the substrate. It was difficult in spite of very numerous attempts to find a substance which possessed all of these properties at the same time and in addition had a vapor pressure of about 1/100 mm Hg. We mention a few small examples: glycerine, (too low vapor pressure), decaline (too high vapor pressure), α - bromonapthalene (no coherent layer), ethylene glycol (slight swelling of the membrane), benzo-acid ether ester (destroys the membrane), etc.

Therefore at least one of the named requirements must be relaxed. So far all infrared photographs with liquids have been made with mixtures, and in particular specially prepared[2] narrow petroleum fractions have been used. Mixtures of numerous members of the series $C_n H_{2n+2}$

[1]A few attempts to replace the zapon-lacquer membrane by other material or to protect it from chemical action by a thin quartz overlay (compare H. C. Burger and P. H. van Cittert, Zeits. f. Phys., 66, 218, 1930) have not yet been successful.

[2]In the laboratory of Dr. Fraenkel and Dr. Landau, Berlin-Oberschoenewerde.

and one fraction in particular have been used. Their boiling points are from 260° to 280° C at one atmosphere.

These fractions had the above disadvantages and a few more: The most volatile components which have become fractionated during operation do not take part in the process on the membrane, but quickly raise the pressure in the chamber so high that the diffusion velocity of the other molecules is extraordinarily strongly reduced (a very undesirable "desensitization"). Thus a trap must be used: a third hole of the stopcock manifold leads downwards to a small blind sack(diameter ~ 0.8 cm, length 10 cm) which is cooled with liquid air. This method of operation, unfortunately, means a further departure from the ideal equilibrium state as it is hoped for and as it was nearly reached in the original use of napthalene.

In spite of the disadvantages of such mixtures -- designated oils for short in what follows -- good progress has resulted. The sensitivity is about 50 times that of the napthalene layers: a Hefner candle at a distance of 2 m gives a clear color change in about 2 minutes, which is to be expected in about 1 1/4 minutes according to calculations, assuming no energy loss. It should be noted as a limit that, for example, a 1/2 Hefner candle at the same distance does not produce the same color change in four minutes, but in an appreciably longer time. It is to be expected that these are of secondary origin and can be minimized by the use of chemically pure substances and the best membranes. Provisionally it would seem that the value of long exposures is illusory.

A further important point is the attainable resolution. It was to be feared that the heat resulting in the absorbing soot layer[1] would be greatly divided by lateral conduction before it could be used for evaporation, for the most heat is produced in the part of the absorbing layer farthest removed from the membrane, on the side where the radiation falls.

The greatest part of the heat produced must therefore first penetrate almost the entire soot layer, before it reaches the membrane with the

[1]Systematic investigations with other absorption materials, such as bismuth-black or silver-gelatine emulsion, have not been made.

condensed layer. During this flow naturally much of the heat also flows to the sides. For fine work one must give up all hope of energy gain and work with thin soot layers, which for example only absorb 50%, rather than with twice as thick a layer, which only absorbs 25% more but conducts much more strongly. The highest possible value of the absorption constant γ is very desirable. γ soot falls off quickly at longer wavelengths, so that in the middle infrared other absorbers should be sought. In order to determine the lateral conductivity quantitatively, a system of 21 lines was produced on a silvered glass plate by a dividing engine. The individual lines had a width of 1/10 mm, the 20 spaces were 20/100, 19/100, 18/100 ------ 1/100 mm (Figure 5a, about 2.7-times natural size. The last three lines are not resolved). The entire system was therefore $21 \times 1/10 + 20/2\ (1/100 + 20/100) = 4.2$ mm wide. From this apparatus 1:1 infrared photographs were produced, of which one is given in Figure 5b, likewise about 2.7 times magnified. One can easily detect the spaces to about 9/100 mm width. The infrared membrane thus corresponds to a photographic plate with granularity of about 1/20 mm = 50 μ. If required one can go further by very complete adjustment and the use of the thinnest possible soot layers.

The resolution reached here is however adequate for many infrared spectrum pictures. Moreover there always remains the possibility of increasing the slit width and the dispersion equally to magnify a desired amount; then the necessary radiation time remains unchanged, and one obtains a correspondingly wider spectrum, which is of equal value to that of the original, smaller optics. Only the registration on the membrane becomes more exact, "relatively sharper". The lateral flow in the liquid layer falls off very rapidly at the same time as the lateral heat conduction in the soot. In fact a double dispersion reduces this effect to 1/16. In the case of the resolution obtained, one must for example always choose the dispersion so great that with a slit width of about 1/10 mm all desired isolation will occur in the spectrum.

A few practical uses of the infrared photography have been made to test their usefulness in a few characteristic examples. The first attempt was to obtain the spectrum of a Hg arc lamp. Figure 6 shows one such picture from 4358Å into the infrared, with an exposure of about 2 minutes

with a very wide slit (0.4 mm) using a 60^{o} quartz prism of 5×5 cm^2 surface area. A mirror spectrometer of Schmidt and Haensch (diameter and focal length of the mirror 4.9 and 34 cm) was used to obtain this picture as well as those which follow. Five lines or line groups can be seen:

4358 5461 5791 10139 11290 .

The spectrum is faint and not sharp, since the oil layer slowly became rather uneven (flecked) during the irradiation and then did not show clear interference color. This disturbance has been very frequent and has its source in small unevennesses of the zapon-lacquer surface, which can probably be reduced by changes in the lacquer mixture; meanwhile they are very disturbing. (On other substrates, for example glass, the oil layer remains completely clear.)

It is to be noted here that the contrast on the photographic plate - in the case of the simple illumination described above - is of course only a partial measure of the thickness differences and therefore of the intensity of the individual lines. However, with monochromatic light this sort of intensity measurement is possible: one evaporates enough oil on the membrane that minimum reflection is obtained at the observation frequency. A spectrum then appears as bright on a dark background, and the brightness is a monotonic (even if non-linear) measure of the intensity of individual lines, as long as the strongest line does not go past maximum reflection.

It is obvious that one can obtain the same spectrum as dark lines on a bright background by so evaporating on the membrane before exposure that it shows maximum reflection. Thus it was, for example, in the Hg picture. There is no point in distinguishing between negative and positive in this method of interference colors.

In an attempt to photograph the known rotation-vibration band of HCl at 3.46 μ, a small cylindrical absorption tube of 10 cm length and 4 cm diameter, closed on the front sides by mica plates, was filled with HCl gas at one atmosphere. A Nernst burner served as a source, as in all the following spectrum pictures. It was immediately evident that the entire spectrum was faintly channelled with interference minima of the somewhat too thin mica plates (Compare Schaefer-Matossi, Das ultrarote

Spektrum, Page 143). This sort of disturbance, which can be noticed at first glance with photography, can only be detected much later or be seriously misleading in the case of pointwise measurement of the spectrum. The mica plates were replaced with thicker quartz plates and the HCl band was obtained. Figure 7 is produced with a poor membrane. One can however detect several lines (bright on a dark background) of the HCl rotation-vibration band at 3.46 μ among a few H_2O and CO_2 bands. Figure 8 shows another clearer picture of the HCl band alone, slightly magnified. (Dispersion in both cases: a 60^o quartz prism + a 60^o Ca F_2 prism 5×5 cm^2. The latter could also be dispensed with). Irradiation time about 3 to 5 minutes.

For comparison with the spectra photographed by the specific absorption in napthalene[1] we produced photographs using oil layers on the one hand, and on the other the napthalene spectrum was measured in the usual way, with a micro-radiometer. For both purposes clear napthalene plates were used, cut from the frozen surface of a napthalene melt. These plates were of different thickness (0.1 to 3 mm) and were placed in front of the entrance slit of the prism spectrometer. For the measurements with the microradiometer a C_aF_2 prism of 54^o angle and 4×5 cm^2 surface was used. The slit and napthalene plates had the following measurements:

λ in μ	1 - 2.5	2.5-5	5-7	7-9
Slit width in mm	0.05	0.2	0.6	1
Plate thickness in mm	3 and 0.5		0.2	0.1

The measurements are given in the curves of Figure 9 and show good agreement with the spectra of Figure 11 and Figure 12.

Figure 10 shows the continuous spectrum of the Nernst burner with the absorption lines of H_2O and CO_2. (No absorption was observed due

[1]M. Czerny, loc. cit.

to the oil vapor in the chamber). In this picture the CO_2 band at 4.27 μ appears bright on a dark background while the other absorption line at 2.6 μ appears dark on a bright background. For a reason, one remembers the very strong evaporation of the oil layer in the short-wave length region, up to about 3 μ. The slit width was about 0.2 mm, the exposure time a few seconds.

Figure 11 shows the absorption of a very thin napthalene plate (about 0.1 mm, slit width and exposure time as in Figure 10). Therefore we see, in addition to the previous spectrum, only the strongest absorption lines of napthalene at 3.3 μ, between 5 and 6 μ, and at 6.3 μ. As a completion to this, Figure 12 gives, with greater dispersion (60^o quartz prism) and somewhat narrower slit (about 0.15 mm), the shorter wavelength, weaker napthalene absorption lines of 1.7 to about 2.8 μ with a thicker plate (0.5 mm). Exposure is about one minute. All these spectrograms show very clearly the dominant intensity in the neighborhood of 1.5 μ. Here the layer is always completely evaporated if the longer wavelength part of the spectrum appears at all.

The abolition of the second spectrometer slit is an advantage under otherwise similar conditions, since the second slit with its finite width contributes to smoothing out the curve. Only with slits which are less than about 0.1 mm is this advantage of the photographic method compensated by the division of heat in the soot layer.

A further possible use of infrared photography aside from spectrography is the imaging of hot objects by their radiation. In principal every radiating body can produce an infrared picture as long as its temperature T_1 is higher or lower than room temperature T_0. With the help of the Stefan-Boltzmann law it is possible to calculate for a given temperature the exposure τ which is necessary to give a strong color contrast, and therefore a clear picture of the object.

Assuming no losses, complete blackness (emissivity = 1) for object and membrane, and an opening ratio (mirror diameter d: picture diameter b) of 1:6, the following exposure times τ are necessary for a color differentiation:

T_1 in °C	-273	0	+10	16	20	60	100
τ in min.	0.1	0.5	1.3	7	2.5	0.13	0.05

(Room and membrane temperature T_0 = 17°C)

In general the loss due to not having black bodies is not greater than about 50%. The illumination times are therefore quite short and allow a good usefulness of the infrared photography for many investigations in heat technology, for example, to obtain the temperature distribution of bodies which are not easily gotten at, with which a point-by-point measurement with a thermocouple is difficult or impossible. Figure 13 shows as an example the infrared photograph of a strongly heated (4 watt[1]) anode of a rectifier (Telefunken RGN 1504). The exposure time was only a few seconds, although the anode had a smooth surface and therefore a very low emissivity. The membrane used showed a few disturbing flecks and the oil layer a rather flecked surface, so that the picture is not satisfactory to give a picture of the temperature distribution on the anode. However, for this it is only necessary to improve the technique. The ends of the three filament wires appearing above and below the anode appear unnaturally brightened, since they radiate most strongly. These spots are thus "over-lighted". For this the filament was underheated (2.0 volts instead of 2.5 as is normal) and was visible only in the center, which is completely covered by the anode.

Moreover it can be clearly seen that the smooth metal surface which radiates weakly departs most strongly from the Lambert's cosine law for strip emission; the oblique small walls of the anode (from which the side wings go) radiate most strongly.

Figure 15 shows a radiator at about 90°C, a blackened glass flask filled with hot water. Optics used, b:d = 6:1; exposure about one half minute (calculated, about 4.5 sec). The reason for the low efficiency lies chiefly in the very incomplete blackening of radiator and absorber; moreover the loss at the mirror is important. Figures 14 and 16 show the objects used in making the pictures in Figures 2, 13, and 15.

[1]Even at an anode power of only 0.5 watts, a picture (although very incomplete) was obtained after a few minutes.

The exposure time is chiefly limited by the impurity of the evaporated substance and the small irregularities of the zapon-lacquer membrane, as described above.

However, after solving these more technical difficulties it should be possible with the resolution and sensitivity attained to obtain spectrograms with this method in measurable exposure times which are of greater ease of solution than with the ordinary radiation measuring instruments. For the latter are in general used at the limit of Brownian molecular motion. Right here lies one of the most important advantages of the photographic method, since it can integrate out the effects of this sort of fluctuation and accumulate the effects of the radiation[1]. Also variations in source intensity are not a disturbance.

I owe great thanks to Prof. M. Czerny who suggested this problem, for many valuable discussions and for his great interest in the progress of the investigations. I thank Geheim Prof. Nernst for providing the facilities of the Institute for carrying out the work. I thank Privatdocent H. Fischer of the Chemical Institute of the University of Berlin for his friendly advice and assistance in the choice of organic substance.

[1]And indeed theoretically, for an arbitrarily long time, while the other instruments can do this only incompletely until they reach the limits of their deflections (see, e. g., a paper by M. Czerny soon to be published).

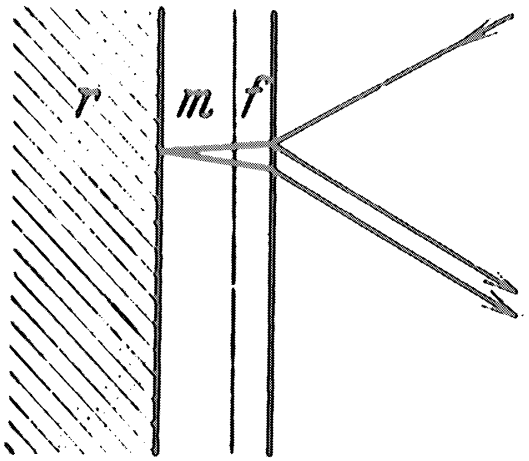

Figure 1 - Path of rays in the production of interference colors on the thin zapon-lacquer membrane.

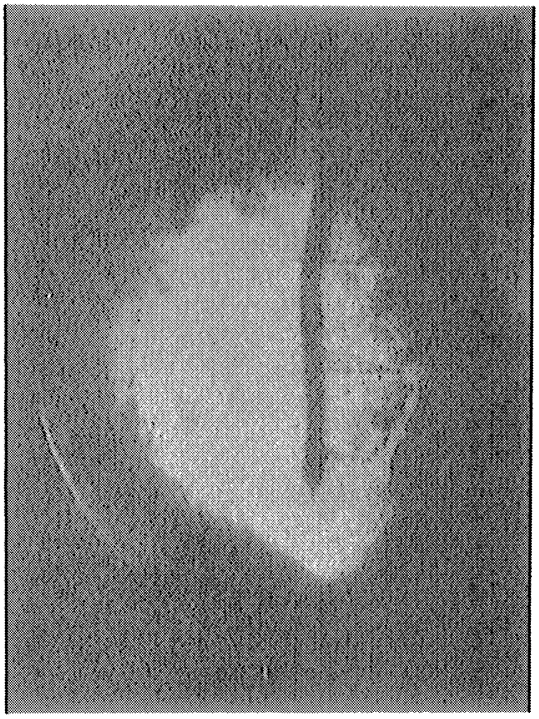

Figure 2 - Infrared shadowgraph of a sheet of lead in the form of a swallow-tail (compare Figure 16) taken with an oil layer which was produced by treating the membrane with heavy oil.

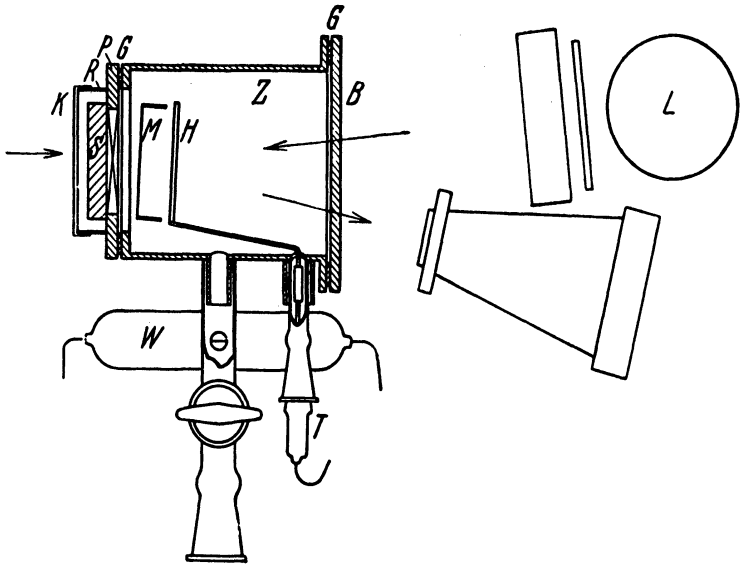

Figure 3 - The Camera

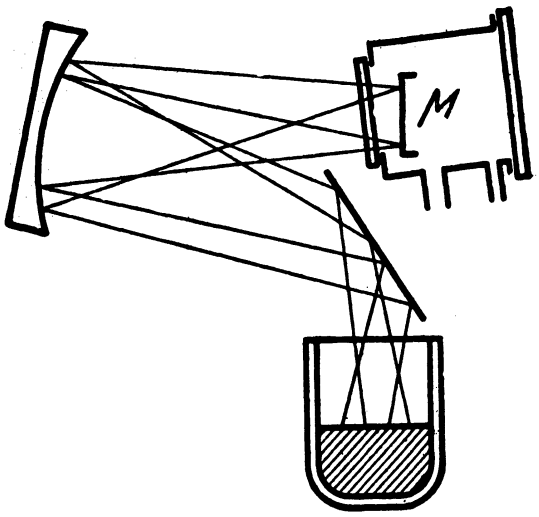

Figure 4 - Cooling of the membrane M, in order to produce a layer by irradiation from a vessel filled with liquid air (note, this figure is referenced in the footnote on the same page discussing liquid air and solid CO_2).

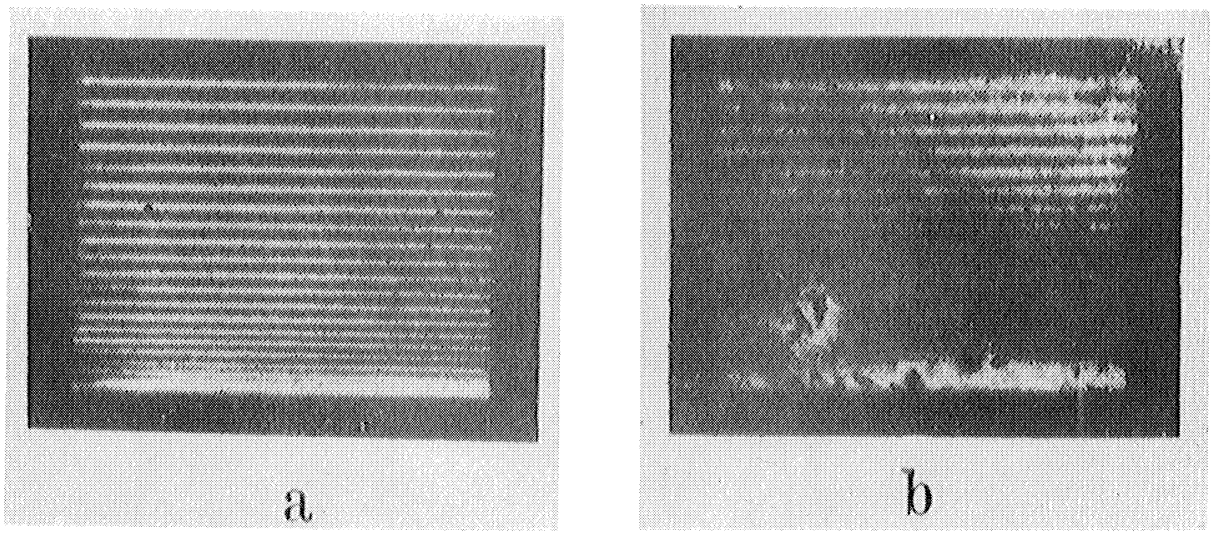

Figure 5 - Line rasters for the determination of the obtainable resolution, a) normal photograph 2½ times magnified (in German text); b) infrared photograph 1 to 1. Afterward magnified 2.7 times for the reproduction (in German text).

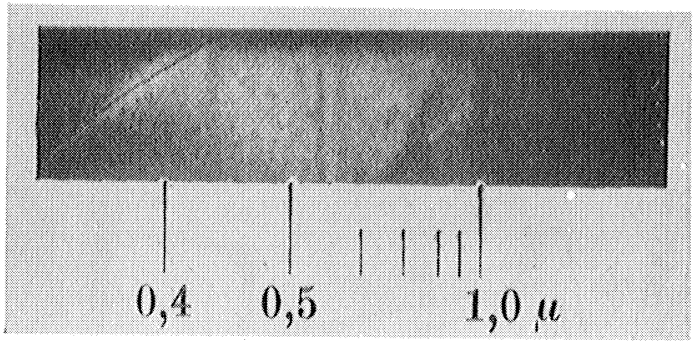

Figure 6 - Emission lines of a mercury vapor lamp. Slit 0.4 mm.

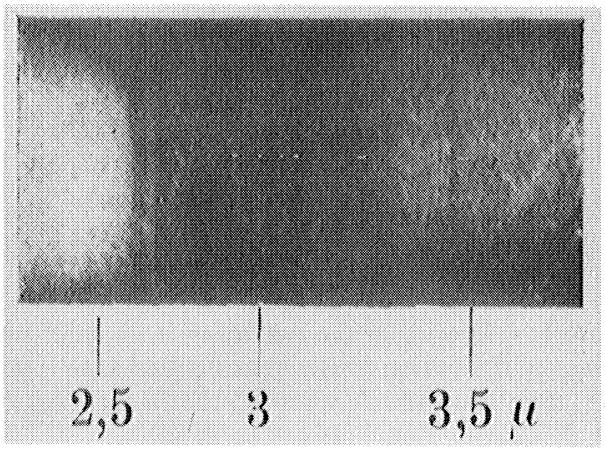

Figure 7 - The rotation-vibration band of HCL gas at 3.46 μ. In addition a few CO_2 and H_2O bands.

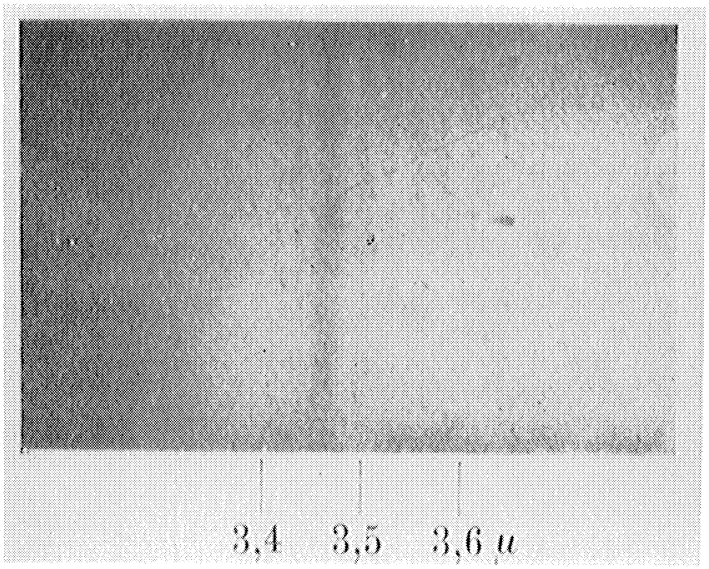

Figure 8 - The HCL band alone.

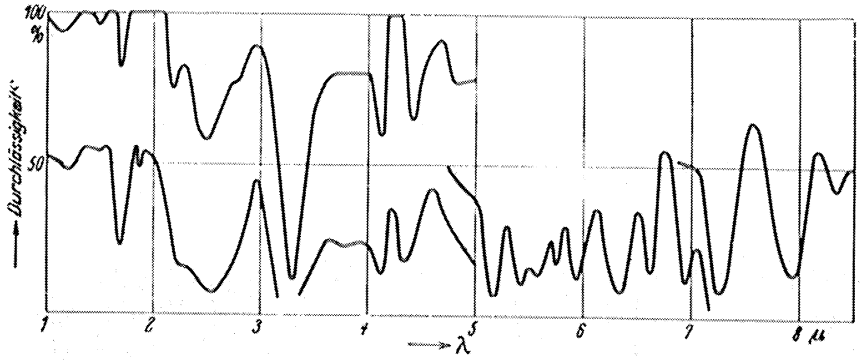

Figure 9 - Transmissivity curve for napthalene measured with a microradiometer.

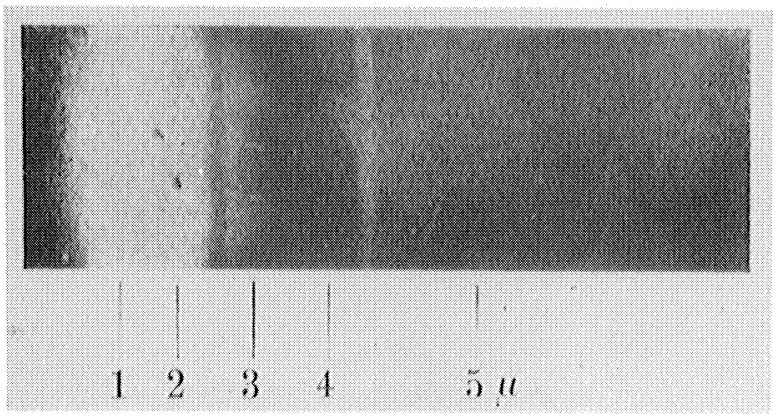

Figure 10 - Chief absorption bands of room air. Irradiation a few seconds.

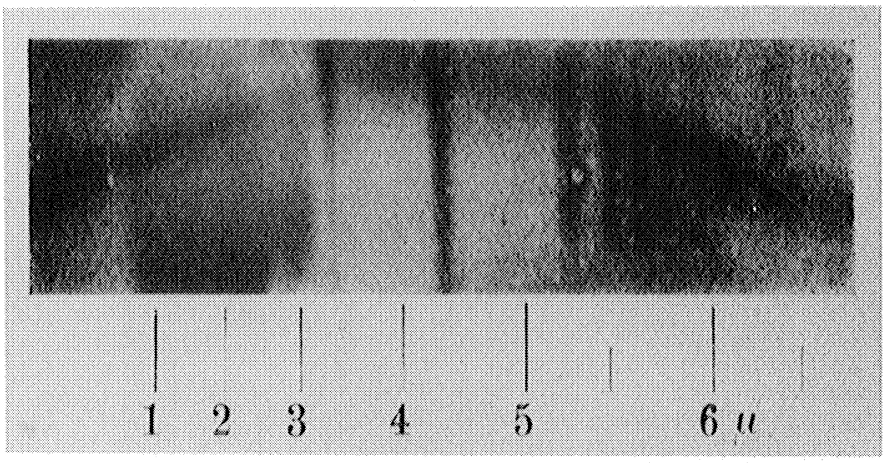

Figure 11 - Absorption spectrum of napthalene between 2 and 6.5 μ. Irradiation, a few seconds.

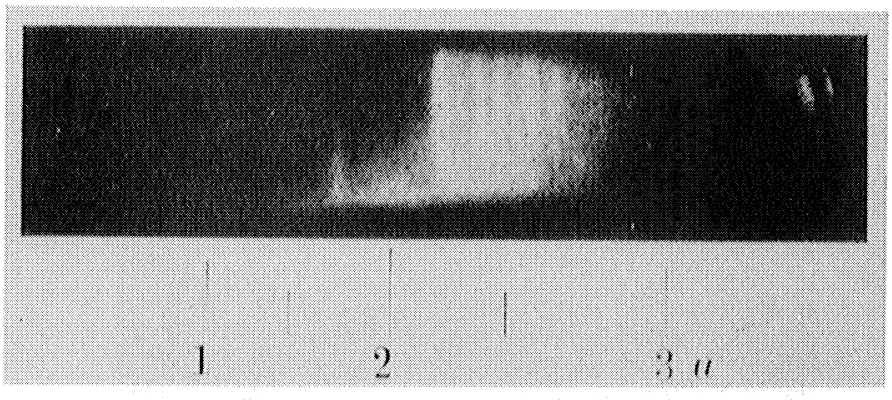

Figure 12 - Absorption spectrum of napthalene between 1.5 and 3 μ, after approximately 1 minute.

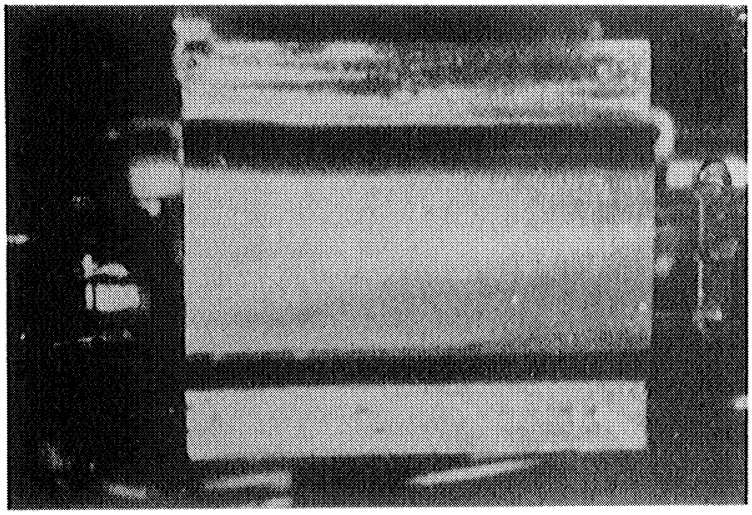

Figure 14 - Ordinary photograph of the anode used. Magnification 1 to 1.

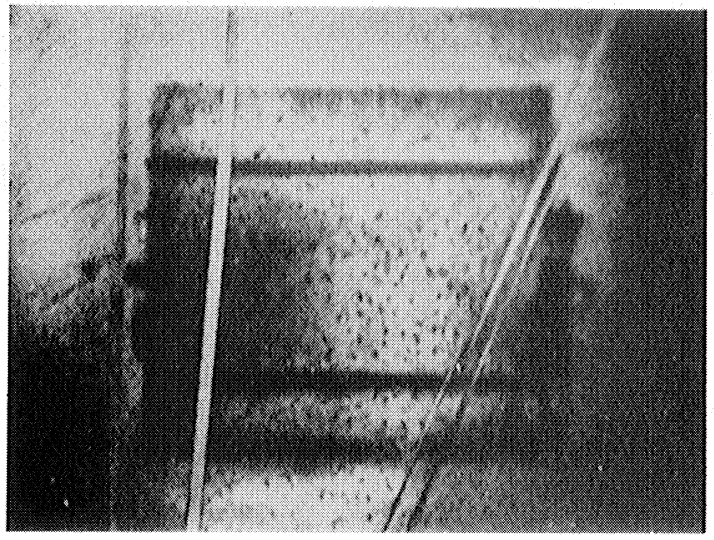

Figure 13 - Infrared photograph of an anode with the help of its natural infrared radiation. Irradiation time, a few seconds.

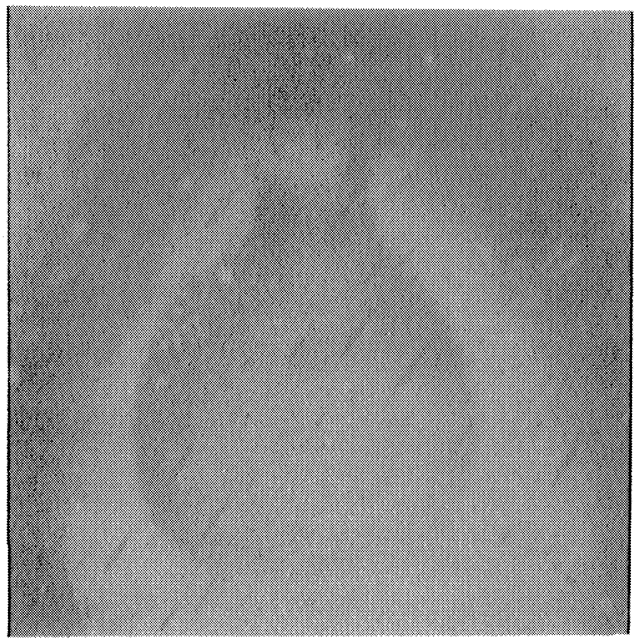

Figure 15 - Blackened glass flask filled with water at 90° C taken with the help of its natural irradiation. Exposure about 30 seconds.

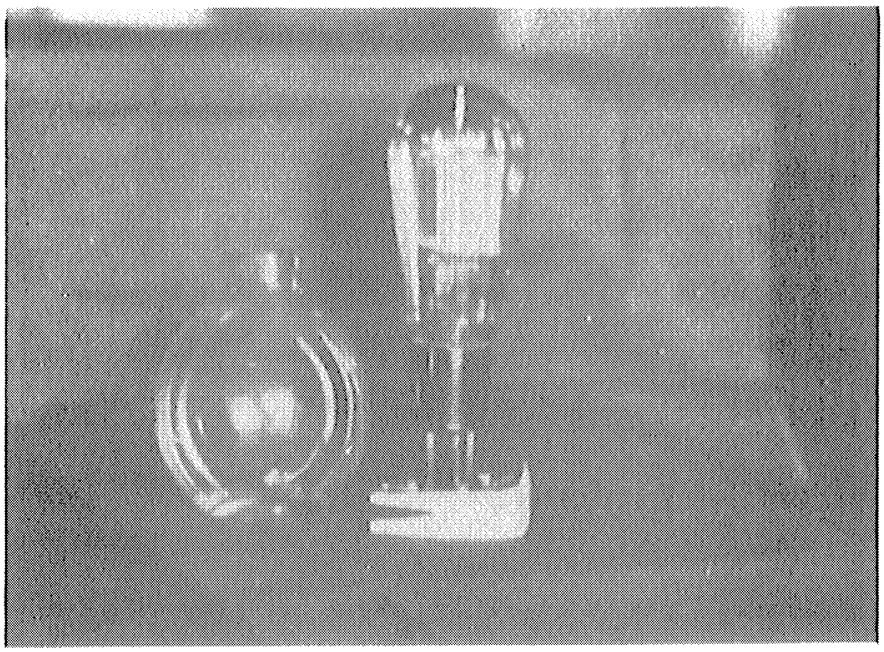

Figure 16 - Objects used in Figures 2, 13, 14, 15.

2144-2-S

INFRARED PHOTOGRAPHY

G. Moench and H. Willenberg,
Zeitschrift für Physik 77, 170, 1932

Translation by L. Tiffany

ABSTRACT

A technical improvement is given in the production of plates for infrared photography (using the Czerny method).

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As a continuation of the previous investigations on infrared photography,[1] a technical perfection of the three-part (support, absorber, and oil layers) photographic plate was sought. These attempts are given in the following:

1. THE SUPPORTING LAYER

As was mentioned earlier[2] there quickly appear disturbing differences of thickness of the evaporated oil layer, which appear visually as mosaic-like color flecks lying on one another. Two possible mechanisms suggest themselves. Either the color flecks result from random accumulations of oil due to statistical variations or result from inhomogeneity of the membrane. In the first case it would be an essential failing of the method, in the second only a technical imperfection. Tests showed that to every source of disturbance belongs a disturbance kernel; the flecks therefore are due to inhomogeneity of the membrane. These nuclei could be particles of dust lying on the membrane, bubbles, or inclusions in the membrane.

[1] M. Czerny, Zeits. f. Phys. 53, 1, 1929; H. Willenberg, Zeits. f. Phys. 74, 663, 1932.

[2] H. Willenberg, Zeits. f. Phys. 74, 674-675, 1932 (see also Fig. 13 of that report).

The photographs show a particularly bad section of a zapon layer by transmitted light and by reflection both with and without an oil layer (magnification 30X). The small disturbed spots in the membrane become large color flecks on oil evaporation. It has been shown that the disturbing nuclei do not arise from the lacquer. Of all the lacquers available the one used thus far, Z116 of the firm I. G. F., Abteilung Filmfabrik Wolfen, appears to be best. The only means of reducing the number of disturbance centers seems to be the production and storing of the membrane in air that is very free of dust. It is recommended also that the membranes be produced at lower water temperatures. The lacquer will then freeze more slowly, allowing more time to spread out evenly. Especial precautions, such as production of the membrane with reduced pressure, has only increased the disturbing sources. Probably this is due to the production of inequalities due to inclusion of water drops.

2. THE OIL LAYER

We have discussed earlier[1] the properties, difficult to fulfill, which a suitable liquid must have and which show the inadequacy of the petroleum fraction used until now. It was also mentioned that the use of a chemically pure substance promised better results than did the mixture used.

The new substance which has been investigated is the saturated hydrocarbon[2] C_{14} H_{30} (normal). In contrast to the petroleum fraction it has a definite vapor pressure; the former especially disturbing volatile components are completely lacking and the sensitivity is constant without pumping.[3] Contrary to expectations these C_{14} H_{30} layers disappear without irradiation about as fast as the earlier petroleum layer. Perhaps the preparation is not sufficiently pure.

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[1] H. Willenberg, Zeits. f. Phys. 74, 668-672, 1932.

[2] Produced by the firm of Dr. Fraenkel and Dr. Landau in Berlin - Obershoenweide (also the less volatile C_{16} H_{34} was considered).

[3] H. Willenberg, Zeits. f. Phys. 74, 672, 1932.

3. THE ABSORPTION LAYER

The absorption layer has so far been produced on the back side of a water-cooled zapon-lacquer membrane by smoking in an open petroleum (kerosene) flame. This method usually results in uneven deposits, whose design changes under infrared irradiation and often leads to deceptive additional figures. Aside from the uneven layer thickness, at times there are small deposits of the cooling water left on the unsmoked side of the membrane, as a result of which the evaporated oil film becomes uneven.

All these disadvantages are alleviated by blacking with bismuth according to the method of Pfund.[1] Without special cooling of the zapon membrane, the black is evaporated in a vacuum of 0.25 mm Hg pressure from a tungsten boat filled with bismuth. The back of the membrane is protected from disturbing condensation.

In addition to the properties of evenness and cleanliness, the greater absorptivity of the bismuth black in the infrared is important. The transmissivity of flame soot in the region of 20 to 130μ is 20 to 40 per cent greater than that of bismuth black, according to Barnes.[2]

The method of blacking by evaporation represents an important advance in the elimination of errors in the preparation of photographic plates.

The investigations discussed here, leading toward technical perfecting of the infrared photography, could not, due to external circumstances, be carried as far as was originally planned. They are therefore neither final nor complete.

We thank Prof. Czerny for suggesting and furthering the investigation, and Prof. Pringsheim for providing the facilities of his laboratory.

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[1] A. H. Pfund, Rev. Sci. Inst. 7, 397, 1930.

[2] R. Bowling Barnes, Phys. Rev. 39, 574, 1932.

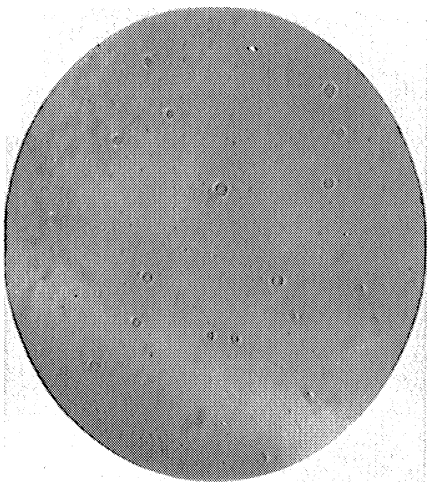

Figure 1 - Zapon membrane as seen by transmitted light.

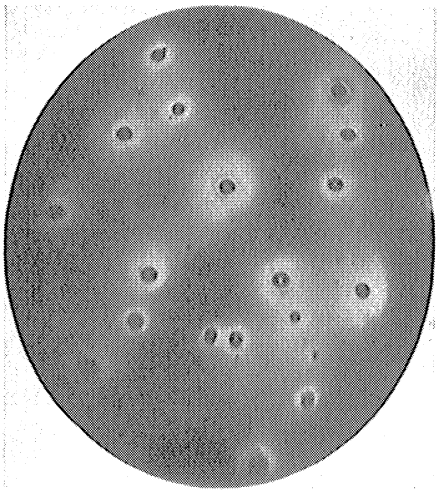

Figure 2 - Zapon membrane as seen by reflected light without oil.

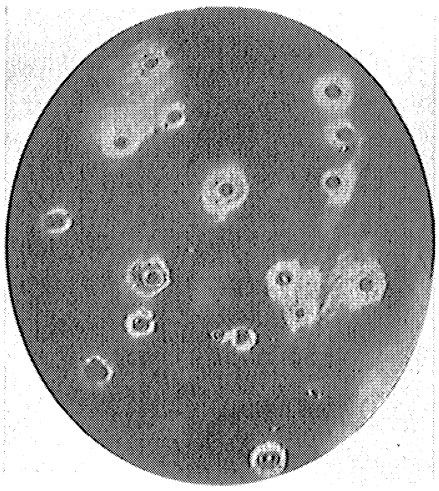

Figure 3 - Zapon membrane as seen by reflected light with oil.

NEW EXPERIMENTS ON INFRARED PHOTOGRAPHY

M. Czerny and P. Mollet
Zeitschrift für Physik, 108, 85, 1937

Translation by L. Tiffany

ABSTRACT

In previous papers a method of infrared photography was given which makes the irradiation visible by means of the evaporation of a substance from the spot struck because of the heat action of the infrared rays. In the present paper we will consider the extension of the method to a practical, useful apparatus. A comparison will be made with the former instrument and a few absorption spectra shown in the region from 1 to 10μ.

In 1929 a method was presented which in a certain sense permits photography with arbitrary infrared rays.[1] It depends essentially on the use of an easily sublimed or evaporated substance which makes visible the spots struck by rays, due to the evaporation of the substance from that spot. The method was developed in important particulars in a dissertation by Willenberg.[2] It was shown that useful results could be obtained with the method. As a result of external circumstances the experiments were then broken off and were first begun again in the past year.

As was presented in the first paper a limit exists in principle for the sensitization of the ordinary photographic plate in the infrared. The more a plate is sensitized for long waves the more quickly it fogs. The black radiation at room temperature contains almost no quanta which belong to the visible spectrum region. On the contrary, the number of quanta rises extremely fast as soon as one goes into the infrared spectrum region. Indeed, one can say with some assurance that the usual

[1] M. Czerny, Zeits. f. Phys. 53, 1, 1929.

[2] H. Willenberg, Zeits. f. Phys. 74, 663, 1932.
G. Moench and H. Willenberg, Zeits. f. Phys. 77, 170, 1932.

limit between visible and infrared spectra, considered at first as simply a physiological matter, has indeed a further meaning.[1] If the eye were slightly more sensitive in the infrared, then in darkness a disturbing diffused brightness would be obtained which is due to the black radiation in the eye (at blood temperature). In the case of infrared plates which can be obtained in the market, those sensitive to the longest wavelengths must be kept under refrigeration. One can see, therefore, that one is already close to the limit mentioned. The plates have their maximum sensitivity at 1.05μ and are usable to 1.2μ with difficulty. Scarcely one octave of the infrared can thus be used for ordinary photography while the totality of the spectrum region designated as infrared amounts to perhaps nine octaves.

All instruments used for the far infrared first absorb the radiation and then measure the heat produced. It is known that these instruments have been developed to the limit which has been set by thermodynamic fluctuation phenomena. Further progress can be achieved with these only through the method of permitting the energy flow of the radiation to be collected over longer periods of time.

Since the new method of infrared photography seems to be promising in both these respects, namely reduction of the disturbing influence of the black radiation at room temperature and longer accumulation time, we have carried the experiments further.

The essential feature of the method consists in the fact that a celluloid membrane of perhaps 1/10μ thickness is covered on one side with a substance which absorbs the infrared radiation. Soot, bismuth black, or very thin metal sheets may serve for this. On the other side of the membrane, a layer of paraffin oil is deposited which is so thin that the paraffin oil layer together with the membrane gives a satisfactory and as even as possible interference color in reflected light. If radiation falls on one spot of the membrane then the spot becomes warmer than the surroundings. Some paraffin oil evaporates from the spot and the interference colors change on this spot. This very sensitive color change can either be detected by the eye or, if a fixation is desired, photographed with an ordinary plate. The deposition of the

[1] M. Czerny, Zeits. f. Techn. Phys. 14, 440, 1933.

paraffin takes place several orders of magnitude more quickly if one carries out the experiment in a volume from which the air is removed and which has the pressure only of the saturation vapor pressure of the paraffin oil (approximately 0.01 mm mercury). By admitting some air one can effectively desensitize the process if one wishes.

1. THE CAMERA

The apparatus developed for the following experiments in conjunction with Willenberg is shown in Figures 1 and 2. In Figure 1, the celluloid membrane M is placed in a brass container G. On the right side the container is closed with an infrared transparent window; on the other side it is closed with a thick plate-glass plate. The closing plate is fastened to the brass ring by rubber rings as is done in kitchen preserving. The membrane is cemented to a brass ring r with picein (free opening of the ring 68 mm). The ring is carried on three points by a small halter. It is important that the fastening between membrane and container wall have as small a cross-section as possible in order to prevent paraffin oil from creeping over from the wall to the membrane. The measurements of the container may be taken from the figure. The air is removed from the vessel by a one-stage rotating oil pump and a one-stage mercury vapor pump without a cooling trap. (A two-stage rotating oil pump alone would probably be sufficient and simpler.) As a vacuum control a hot wire manometer of the simplest sort serves. The strength of the electric heating current at constant voltage serves as a measure for the height of the vacuum.

A vertical, electrically heated, closely wound, spiral wire serves for the evaporation of the paraffin oil. The spiral consists of a resistance wire of 0.15 mm thickness and is fastened to a 0.3 mm thick steel wire by welding. The heating current is approximately 100 ma. The spiral together with the container for the material sits on an arm which can be moved in and out by a glass control. By this means a uniform evaporation on the membrane results. Further, the motion of the spiral to the side permits an unhindered observation of the membrane.

Paraffin oil absorbs a great deal of air. If one evacuates the container with a fresh filling of paraffin oil, then the air is removed in large bubbles from the container V. The paraffin oil runs out in part

and in particular small oil spots may be formed on the membrane which lead to the formation of flecks. It is therefore desirable that the paraffin oil be placed in a special vessel and the air removed before use. One filling of the vessel V is sufficient for perhaps forty evaporations on the membrane.

The membrane covered with paraffin oil shows, at least in the center section, a uniform interference color. When infrared radiation falls upon it, perhaps in the form of a line spectrum, there occur corresponding linear changes in the spectral color. In order to detect these, the surface of the membrane must be imaged by means of an optical system on the eye or a photographic plate. One obtains the best imaging by an optical system whose axis is perpendicular to the center of the membrane. Since the interference phenomena can only be seen in geometrically reflected light the membrane must be illuminated normally from the front with the help of a half-silvered mirror at an angle of 45^{o}. From these considerations one arrives at the paths of the rays represented in Figure 2. As a light source Q_1, an auto head lamp of 6 volts and 6 amperes serves. Its rays pass through two color filter plates (Schott glass BG19, 4 mm thick and BG 7, 1 mm thick). The two filters absorb all of the infrared rays and also absorb the visible rays to about the green.[1] The remaining bluish light is quite bright to the eye and acts strongly on the ordinary photographic plate. However, it does not have a noticeable effect on the infrared membrane. This leads to the observation, which has been shown in other ways, of how little sensitive such a heat detector is in comparison to the methods which use light quanta, such as the photochemical reaction.

The filtered light is made parallel by the condenser lens L_1 (f = 12 cm, diameter 50 cm) and is then thrown from the half-silvered 45^{o} mirror S_1 onto the membrane M. From this it passes back through the mirror and the achromatic lens L_2 (f = 24 cm) to the achromat L_3 (f = 50 cm). A real image of the light source Q_1 is produced by the objective L_3. A real image of the membrane M is produced in the plane P (2-1/2 times magnified); the objective L_2 is placed at such a distance from the membrane that an enlarged virtual image of the

[1] A nearly saturated $CuSO_4$ solution of 20 mm thickness has the same sort of action, although perhaps less reliable.

membrane results and this image is focussed by L_3 on the plane P. A photographic plate or a focussing screen can be placed there. A mirror S_2 can be placed in the path of the rays for direct visual observation. If one places the eye behind the opening A one can see an image of the membrane which is equally bright because the light source Q_1 is imaged on the pupil of the eye.

A disturbing reflection is produced on the glass closing plate of the vacuum container. To reduce this it is sufficient that the vacuum container be somewhat inclined to the closing plate but not to the membrane. The light reflected on the enclosing plate is then intercepted by the diaphragm of the objective L_3.

For convenient orientation in the spectrum it is desirable to project a millimeter scale on the spectrum. Such a scale is shown in Figure 2 at SK. Millimeter marks are scratched on a well blackened surface which is lighted from behind by the lamp Q_2. The scale is placed in such a position with respect to the mirror S_1 that its mirror image falls upon the membrane. The lamp Q_2 takes 1.25 amp. at 4 volts. Between lamp and scale there is placed again a filter glass to remove the infrared rays (Schott glass BG 19, 4 mm thick) and a condenser lens which makes the rays of the lamp parallel.

2. THE PRODUCTION OF THE CELLULOID MEMBRANE

Celluloid membranes are produced on water by the spreading of zapon lacquer.[1] The lacquer spreads itself on the surface of the water, the solvent evaporates and the solid celluloid skin may then be lifted from the surface of the water with a wire frame. This method has the disadvantage that one side of the membrane is always wetted with the water. Many small disturbing bits of salt then remain upon drying even if one uses ordinarily distilled water. Moreover the strain on the membrane is rather great on drawing it out. The following method therefore seems preferable. A wire frame is made according to Figure 13. To a sufficiently regular brass wire of 50 cm length and 5 mm thickness, galvanized iron wires are soldered. If one produces a zapon-lacquer membrane of about 30 cm diameter on the surface of the

[1]As in the earlier works the best zapon lacquer seems to be Z-116 of the Agfa film fabrik Wolfen KR - Bitterfeld.

water and then lifts the frame which was previously sunk in the water so that the brass wire passes from beneath along a diameter, then the membrane on further lifting, folds on both sides over the brass wire. The two membrane surfaces have at first a small quantity of water between them. This runs out and the two surfaces then cling to form one homogeneous membrane. The two outer surfaces of the membrane are always kept dry in this fashion. Since one always forms a double membrane in this fashion the method seems particularly satisfactory in producing thin membranes of greater evenness. For the experiments membranes were used which either showed a nearly colorless iron gray or which were just beginning to show a straw yellow. This corresponds to a layer thickness of 0.1μ and less. In the production and the storing of the membranes, as great care as possible must be taken to ensure freedom from dust.

The water surface used was 56 × 56 cm in size. If a smaller size is used one does not obtain as uniform a membrane. Moreover the zapon lacquer does not spread out to the wall but stops spreading when approximately half of the water surface is covered. For the production of membranes with as few disturbing spots as possible boiled distilled water must be used. In order to place the wire frame in a vertical position in the water without having to use too great a quantity of distilled water a flat four-sided tray of 56 cm length of side was made of sheet German silver.[1] In the middle of the tray a slot 30 × 40 cm was cut and a vessel 11 cm deep soldered into the bottom of this in which the wire frame could be placed.

3. PRODUCTION OF THE ABSORBER LAYER

The membranes are too thin to absorb the infrared rays in any appreciable quantity. Only in the regions of the spectrum in which thick celluloid layers absorb strongly is a rather small effect noticeable with the thin membrane. One must therefore cover one side with a special blackening material. The best results are given by layers of bismuth black. Pfund[2] has shown that if one evaporates bismuth at a pressure of about 0.25 mm Hg one obtains deep black bismuth layers.

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[1]Poor results were obtained with tin plate and sheet zinc probably due to the impurities.

[2]H. Pfund, Physical Review, 35, 1434, 1930 and Reviews of Scientific Instruments, 1, 397, 1930.

Willenberg and Moench have shown in their paper (which has already been cited) the usefulness of these methods of blacking the celluloid membrane. We have carried out the evaporation under a large bell jar. The membrane was placed at about 10 cm distance from the evaporating bismuth. Bismuth particles of about 5 mm diameter were placed on an electrically heated tungsten wire. The gas pressure was controlled through a small discharge tube. The best results are shown at pressures which give a layer discharge in the discharge tube. At too high a pressure one obtains an ash gray layer, in part colored deep black. At too low a pressure one notices the change to a metallic mirror surface. The duration of the evaporation is 4 to 10 minutes. In the case of too strong heating of the bismuth the formation of black clouds can be seen in the vessel. This never gives an even blackening of the membrane. The bismuth black adheres more easily to the membrane if the membrane is cooled on the back. For this purpose a brass plate of 10 mm thickness is placed 5 mm behind the membrane.[1] Figure 4 gives the percentage transmissivity of a few bismuth membranes in the short wavelength infrared. They were obtained with a mirror spectrometer using a sodium chloride prism and a microradiometer as detector. The quick rise of the transmissivity with wavelength is well known but means a complication for the infrared photography. One must use membranes of different thicknesses according to the wavelength region in which one would like to work. The membrane with the lowest transmissivity in the figure is already so thick that it can no longer be used in the infrared photography for very fine resolution. The heat diffuses from the irradiated spot too quickly to the side. In the figure the middle layer shows a good resolution. Of course it could be used because of its sensitivity for longer wavelengths, if it were a better absorber.

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[1]An interesting phenomenon occurs here. The bismuth layer appears inhomogeneous by transmitted light because one notices inequalities which have the form of different lines. It would appear that these lines are the scratch marks on the brass plates even though the membrane does not touch the brass plate. If one scratches a letter or character very gently on the brass surface then it appears in the bismuth layer by transmission. We have not gone into the source of the phenomenon further but have used a well polished brass surface in order to minimize the disturbing phenomena for us.

Only the metals show a capability of absorption in thin layers in the infrared almost independent of the wavelength. For in the far infrared the optical properties of the metal are determined only by the specific electrical conductivity. Woltersdorff[1] has investigated both theoretically and experimentally the connection between the reflectivity R, the transmissivity D, and absorptivity A on the one hand and the thickness of layer d of the metals on the other. We take from their work Figure 5 which gives the theoretical connection between them. As abscissa the thickness d is shown not alone but as the production $\sigma \times d$ in which σ is the specific electrical conductivity of the metal in the absolute electrostatic system. The figure is good in general for all good conductor metals and for all wavelengths in the long wave infrared. It can be seen from this that an absorptivity of 40 to 50 per cent can be expected. The metal layer has a transmissivity of 10 to 60 per cent. Woltersdorff has shown that the values found experimentally in the case of aluminum agree reasonably well with those calculated theoretically. We have made a few experiments with such thin aluminum layers as the absorbing medium.[2] In Figure 6 are reproduced transmissivity curves of a few membranes which were produced in a high vacuum by the evaporation of aluminum. One can see how the variations with wavelength occurring in the short wave infrared are reduced at longer waves. For the practical use of infrared photography such membranes seem to be usable. As far as the experiments have shown until now these layers show only half as good a resolution as the layers covered with bismuth black. The heat conductivity of the metal layer can be noticed readily in the very thin layer thicknesses. Moreover, the control over the sharpness of imaging of a spectrum on the membrane by a mirror becomes more difficult. Furthermore, the interference colors are not as clear as before because the reflection is stronger on one surface than it is on the other. Nevertheless useful results have been obtained, of which one example will be shown in what follows.

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[1]W. Woltersdorff, Zeits. f. Phys. 91, 230, 1934.

[2]These thin opaque metal layers were used for absorbers in the long wave infrared as was previously mentioned by H. Hines. This work is not published however.

4. THE TYPES OF PARAFFIN OIL

Willenberg in his work uses substances which were obtained from raw petroleum by a narrow fractional distillation. Naturally these showed disturbances which were due to the impurity of the substance. He obtained better results in a later work with Moench by the use of a synthetic tetradecane (C_{14} H_{20}). We chose to begin with technical paraffin oil.[1] We repeatedly vacuum distilled the paraffin oil in order to obtain a series of substances of nearly uniform range of properties. During the distillation the vacuum was obtained by a continually rotating oil pump. The paraffin oil and the liquid of the external heating bath were both stirred continually with an electromagnetic stirrer. The progress of the distillation was followed by measuring the index of refraction of the distillate. An Abbe refractometer made by Zeiss was used. The method is convenient but care must be taken that all measurements are carried out under as equal a temperature as possible. A few numbers may serve as examples for the course of the distillation. Technical paraffin oil with slowly rising temperature begins to distill at about 115° and separates into four parts. Only the first and second quarters were worked with further. If the first quarter is again distilled and divided into five parts these parts have indices of refraction n_d = 1.4635, 1.4640, 1.4648, 1.4655, 1.4680. On a further distillation, for example, one can obtain a substance which upon separation in five parts shows the following indices of refraction: n_d = 1.4654, 1.4655, 1.4655, 1.4657, and 1.4670. The substances finally used were obtained from a four or five fold distillation.

By trying the distillate for its properties in infrared photography it was shown that only a rather narrow group should be considered whose index of refraction is in the neighborhood of n_d = 1.4655 at 22° C. Fractions with a higher index of refraction have a lower saturation pressure and therefore work too slowly. On the other hand fractions with a lower index of refraction have the difficulty that they do not deposit as a homogeneous layer on the membrane but give a granular layer. The layer is then flecked with small marks (of the order of magnitude of 100μ) and therefore loses in resolution. Moreover,

[1]The technical preparation had for us the important advantage of being readily available as a pure preparation for medicinal purposes.

the lifetime of layers of these light fractions of paraffin oil is especially low. All paraffin shows, as did also the tetradecane in the case of Willenberg and Moench, the property that the evaporated layer begins to lose thickness and after a few minutes has entirely disappeared. Even when the layer was protected from infrared radiation it was not possible to reduce this phenomenon in such a way as to give the undesirable paraffin fraction layers such a lifetime that, together with a sufficient sensitivity, it could be used for spectrum photographs.

5. SENSITIVITY AND RESOLUTION OF THE METHOD

The measure for the sensitivity of the method was determined by the length of time it took the radiation from the Hefner candle at a definite distance to give a noticeable effect. The vacuum chamber was closed with a 4 mm thick plate of crystalline quartz and in front of this a metal plate was placed with a 10 mm hole. The Hefner candle was so shielded that essentially only the rays of the glowing flame cone were effective, according to the description of Gerlach.[1] The first trace of an image was given in the case of a 1 m distance of the candle in approximately 4 seconds, in the case of a 2 m separation in about 15 seconds, and in the case of the 2.5 mm distance in approximately 25 seconds. The membrane was covered with bismuth black. Naturally the sensitivity depends upon the degree of blackening of the membrane and different properties. The above numbers are approximately the best which were obtained.

In addition it was determined by a rotating sector whether the time to the detection of the first trace of an image was directly proportional to the radiation intensity. If the intensity in such a region was varied so that the first trace of an image was obtained in at most 2 to 4 minutes, the expected dependence was satisfactorily fulfilled. If the intensity of the radiation, however, was much weaker, then irregularities occurred which appeared to depend on the so far unclear phenomenon of spontaneous disappearance of the layer.

A very important point is that of resolution. If one plans to use the method for the taking of spectra, its usefulness depends not only on its sensitivity but also upon the obtainable resolution. The greater the

[1]W. Gerlach, Zeits. f. Phys. 14, 577, 1913.

resolution is, the less dispersion is necessary in the objective or mirror with which one forms the spectrum on the membrane. Such reduction of the dispersion angle leads to an increased energy density on the membrane.

In order to provide a test object for the determination of the resolution three groups of lines were scratched with a needle in an opaque silver layer on a glass plate. The thickness of the silver layer was approximately 40μ. The distance from one line center to the next was approximately 400μ in the first group, 200μ in the second group, and 100μ in the third group. This test object was focussed as sharply as possible in its correct size on the membrane. A light filter was used which only allowed a region of approximately 1 to 2.5μ to have effect. In the case of layers using bismuth black all line groups were completely separated. Figure 7 shows the result of such a photograph. The high magnification was used later for the reproduction. In the case of opaque layers of aluminum as an absorber the 200μ lines were poorly separated; however, the 100μ lines in general were not.

Of course the question arises as to the comparison between the sensitivity of the method described here with that of the experiments carried out before. Such a comparison is quite difficult to carry through strictly. The radiation of a Hefner candle produces a first trace of an image in approximately 25 seconds in the case of 2.5 m distance as we discussed above. If one lets the radiation of a Hefner candle under similar conditions fall upon the cone of a microradiometer one obtains with a scale distance of 5 meters a deflection of the order of 1000 mm. The microradiometer appears therefore at first to be much better. One must remember, however, that the cone of the microradiometer receives the energy stream which falls upon perhaps one square centimeter, while, on the contrary, the membrane, because of its resolution described above of approximately 0.1 mm, can be used with the radiation falling upon a surface of approximately 10^{-4} square cm. Therefore, it can be seen that the energy stream which is sufficient to produce a trace of an image upon a membrane will give only a deflection of approximately 1/10 mm on the microradiometer. As was already discussed the number of such comparisons in their practical meaning can only be taken with the assumption that the infrared photographic method is already about at the limit of the previous

infrared detecting instruments. A chief advantage of infrared photography compared to the previous detector instruments is that it may be used for a longer accumulation time. Unfortunately this has not yet been achieved.

We have also made experiments in order to compare the sensitivity of our apparatus with the photographic plates, obtainable on the market, which are sensitized for the infrared. In order to have a short comparison we will in the following refer to our method as evaporography in contrast to infrared photography with sensitized plates. The experimental setup for the comparison was the following. As a light source we used a Nernst burner (95 volts, 0.95 amp.). For the decomposition of the rays a mirror spectrometer with a 60^{o} quartz prism and mirror of 5 cm diameter and 35 cm focal length was used. Both slits were 0.25 mm wide. The production of monochromatic wavelengths resulted by turning the prism together with a Wadsworth mirror. The second slit was perhaps two times magnified and imaged on the detector layer. In the case of a wavelength of 0.9μ the Schott glass filter RG 8, 2 mm thick was inserted. For longer waves the Schott glass filter RG 7, 2 mm thick was used. For the wavelengths used the filters had a transmissivity of approximately 90 per cent, except that at a wave length of 1.05 mm the RG 7 filter was about 70 per cent transmitting. As an infrared plate we used the furthest sensitized infrared. This plate was the Agfa infrared plate 1050. It was not oversensitized. Development lasted for 3 minutes. The membrane for the evaporography was medium strongly covered with bismuth black.

PROPERTIES OF THE AGFA PLATES

0.9μ	1/25 sec. weak, but clear image 1/5 sec. complete image 1/2 sec. almost total darkening
1.05μ	something like that at 0.9μ (it is, however, to be remembered that the somewhat less transparent filter described above was inserted.)
1.2μ	2 sec. first detection 4 sec. very weak, but clear 8 sec. weak 16 sec. not completely illuminated
1.3μ	16 sec. first indication 32 sec. very weak, but clear 64 sec. weak

PROPERTIES OF EVAPOROGRAPHY

	First trace of image	Usable image		First trace of image	Usable image
0.9 μ	2 sec.	5 sec.	1.5 μ	3 sec.	7 sec.
1.05	3	6	2.0	3	8
1.2	2	5	2.5	7	16
1.3	2	4			

If one remembers, in the case of the above numbers, the possibility of oversensitizing and making longer exposures of the photographic plate, one sees that evaporography is much better than agfa infrared plates in the region for which they were intended. Furthermore, their sensitivity falls off so quickly at longer wavelengths that one should consider the region beyond 1.3 μ as being far better for the evaporograph.

6. A FEW SPECTROGRAMS AS EXAMPLES

As examples of the possibilities of the method in its present state of development the following four spectra are given. These spectra were made with the same apparatus that was used for the comparison of the evaporograph for the infrared photography, that is a Nernst burner and a mirror spectrometer. As a prism either a 60° quartz prism or a 60° rock salt prism was used, each with an opening 5 × 5 cm. The spectra were taken in such a manner that the places which show strong absorption are bright; those places with weak absorption appear dark. In the reproduction the spectra are magnified approximately 2.5 times.

Figure 8 shows the spectrum of liquid methalene chloride ($CH_2 Cl_2$) with a thickness of layer of 1 cm in a glass tube. The spectrometer slit was set at 0.05 mm. A quartz prism was used and time of illumination was approximately 0.25 minute. Methalene chloride shows in this short wave region a particularly rich branched absorption spectrum.

In Figure 9 the well known rotation vibration band of gaseous HCl is shown in the neighborhood of 3.5 μ. Again a quartz prism and a slit of 0.1 mm width was used. The HCl was placed in an absorption tube 10 cm long which was closed with quartz plates. The distance of the

individual rotation lines can be seen to increase in the picture with increasing wavelength rather quickly because the dispersion of the quartz prism is rising in this region. Exposure time--approximately 1 minute.

In Figure 10 a picture is given which was obtained with a rock salt prism and a slit width of 0.05 mm. In the path of the rays of the apparatus only room air was found with its normal content of water vapor and carbon dioxide. One can see in the picture the well known carbon dioxide band at 4.3 μ. The band can clearly be seen in the original plate as a double band although the separation of the two absorption lines amounts only to 0.055 μ according to the measurements of Barker.[1] In the spectrum thrown upon the membrane the separation of two lines amounts to 0.09 mm. This shows that the resolving power of the membrane is here fully utilized. In the long wavelength part one sees a great number of absorption lines which belong to the rotation vibration band of water vapor with a middle point at 6.3 μ. Under a comparator about 25 individual lines can be measured. They show good agreement with the measurements of Bahr.[2] The exposure time amounted to about 1 minute. The short wavelength part of the spectrum is completely over illuminated and therefore shows no individual lines.

In Figure 11 a spectrum of Furfurol ($C_4 H_3 O \cdot CHO$) obtained with a sodium chloride prism and a 0.2 mm slit width is represented. The illumination time was approximately 1 minute. In this exposure a membrane was used on which aluminum had been evaporated to an opaque layer while all the previous exposures were obtained with bismuth black. One can see here a greater number of absorption lines to approximately 9 μ. The lines, however, appear less contrasting and sharp as in the case of the use of bismuth black. The Furfurol was placed as a very thin sheet between two rock salt plates which were pressed together. These show the well known property that for the taking of absorption spectra in the spectrum region only extremely

[1]E. F. Barker Astrophys. Journal, 55, 391, 1922. In the infrared monograph of Schaefer and Matossi a typographical error is given on Page 226 in Table 23. The one absorption line is given as 4.255 μ rather than the correct value of 4.225 μ.

[2]E. von Bahr, Verh. d. D. Phys. Ges. 15, 733, 1913.

small quantities of substances are required.

In examining the different photographs one notices their different amounts of flecks. In general this fleckiness increases with the exposure time. As a source of these small point-shaped flecks we believe there are small disturbance spots in the zapon-lacquer membrane. When viewed against a window a freshly produced membrane appears to be completely clear and transparent. Even under the microscope in indirect light it appears so. However, if one places them under the microscope in intensive dark field lighting, one sees a filling of more or less small scattering centers as illuminated points on a dark background. The more careful one is in the production of the membranes to ensure freedom from dust and other impurities the less one notices such disturbing spots under the microscope and also in the infrared photography. It has not been possible for us, however, to succeed in removing these disturbances. If one lets an intensive light ray fall through the zapon lacquer in its storage container one can see that it is not itself optically clear. Further experiments must therefore have as a goal the production of a completely clear zapon lacquer as an initial material.

Altogether it may be said that the experiments in the present state of development closely approximate the former heat sensitive detectors in sensitivity, but are essentially better in the speed with which a spectrum can be obtained.

For carrying out the preceding work we are indebted to the Helmholtz Fellowship for support for which we owe thanks. Moreover, we have Prof. J. Eggert to thank for the use of photographic plates. Dr. A. F. Turner and Dr. R. Bowling Barnes have given us valuable help in counsel and in deed.

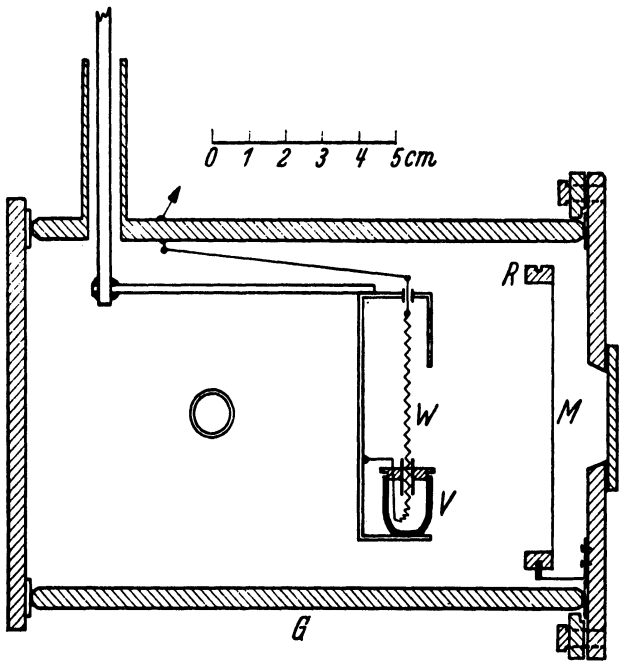

Figure 1 - Vacuum chamber with the membrane M and with the paraffin evaporator W.

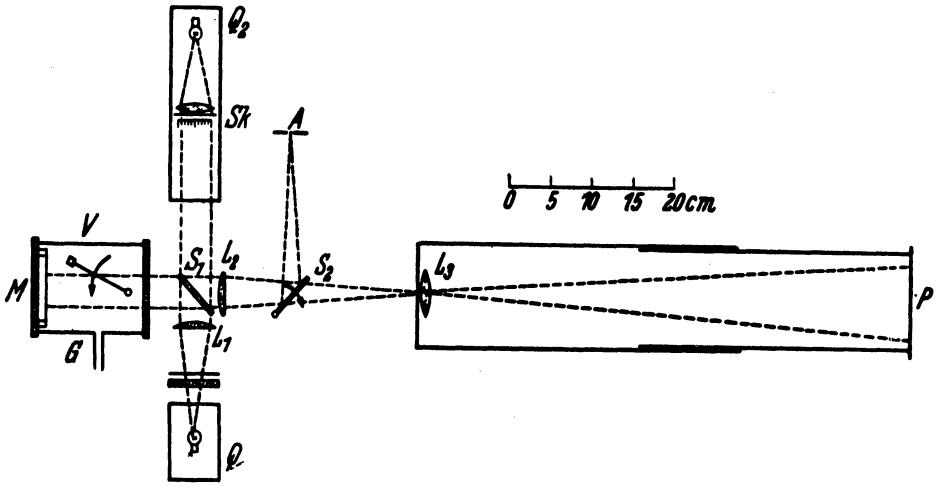

Figure 2 - Apparatus for the subjective observation of the photograph on the membrane M from A, for the photographing of the membrane with the help of the Plate P, and the projection on it of the wavelength scale SK.

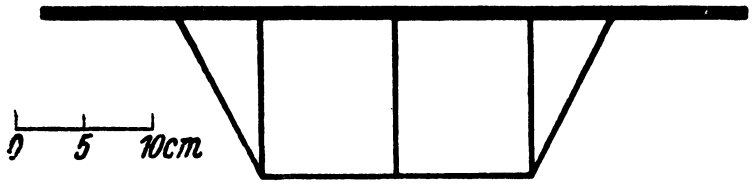

Figure 3 - Metal frame for removing the celluloid membrane of the tank.

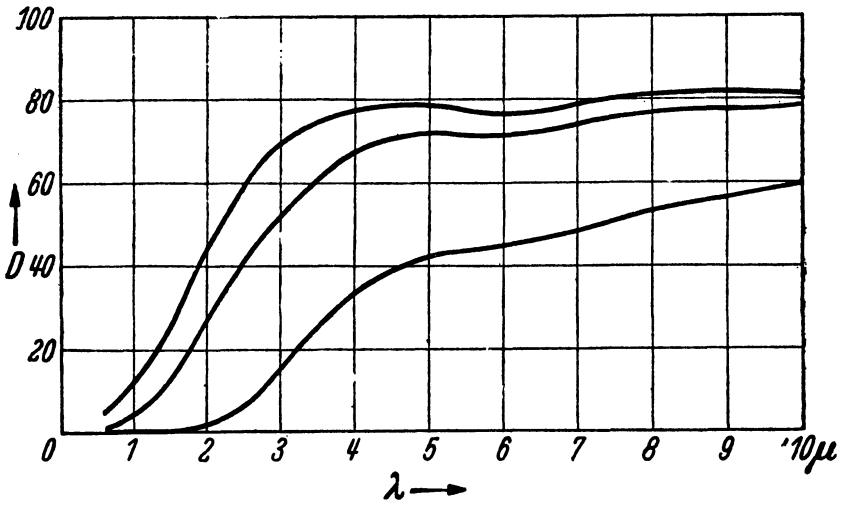

Figure 4 - Spectral transmissivity for three bismuth black layers of different thicknesses.

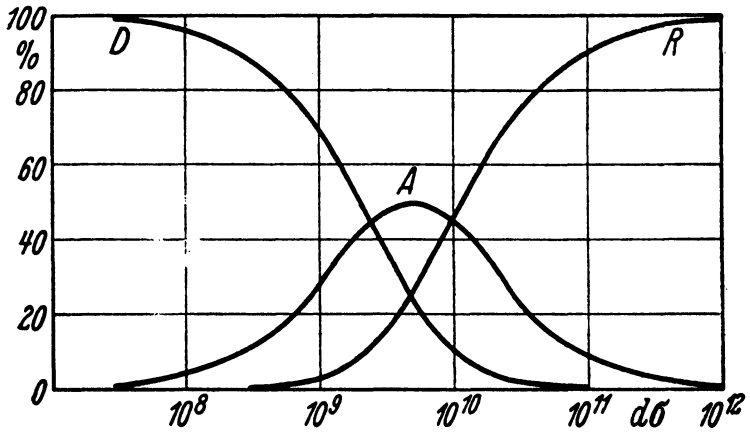

Figure 5 - Theoretical connection between reflection coefficient R, transmissivity D, absorption coefficient A, and the product of the specific electrical conductivity and the layer thickness d. Applicable for all metals in the long wave infrared independent of the wavelength.

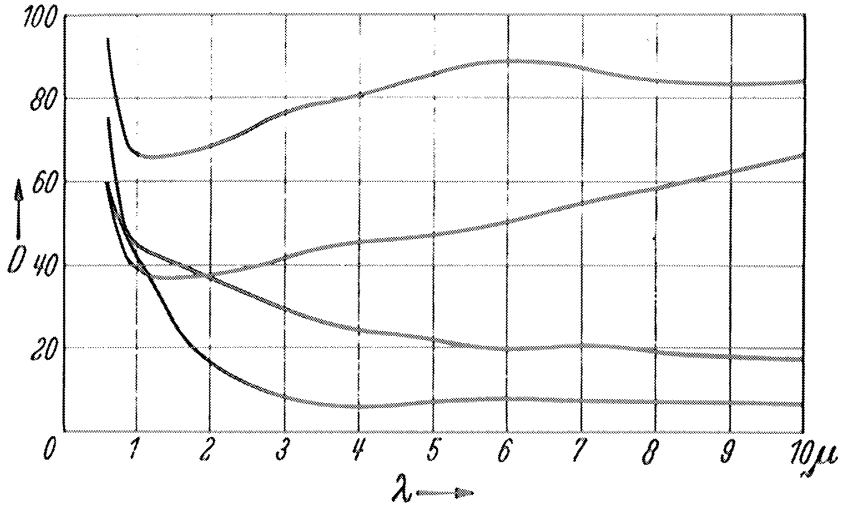

Figure 6 - Spectral transmissivity for four opaque aluminium layers of different thickenesses.

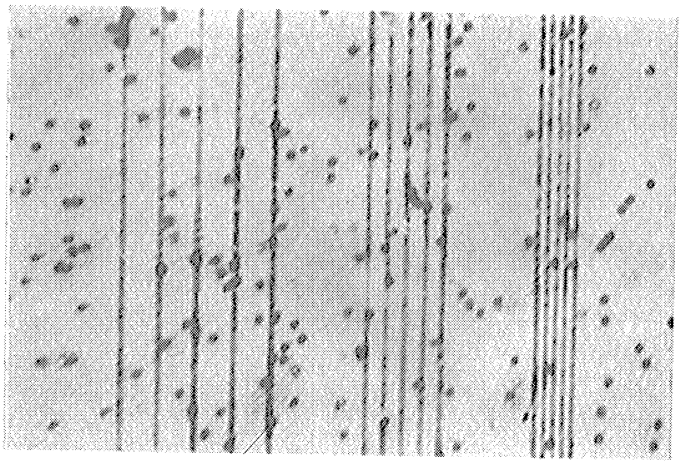

Figure 7 - Test photograph of the determination of resolving power. Line groups with 400, 200, 100 separation.

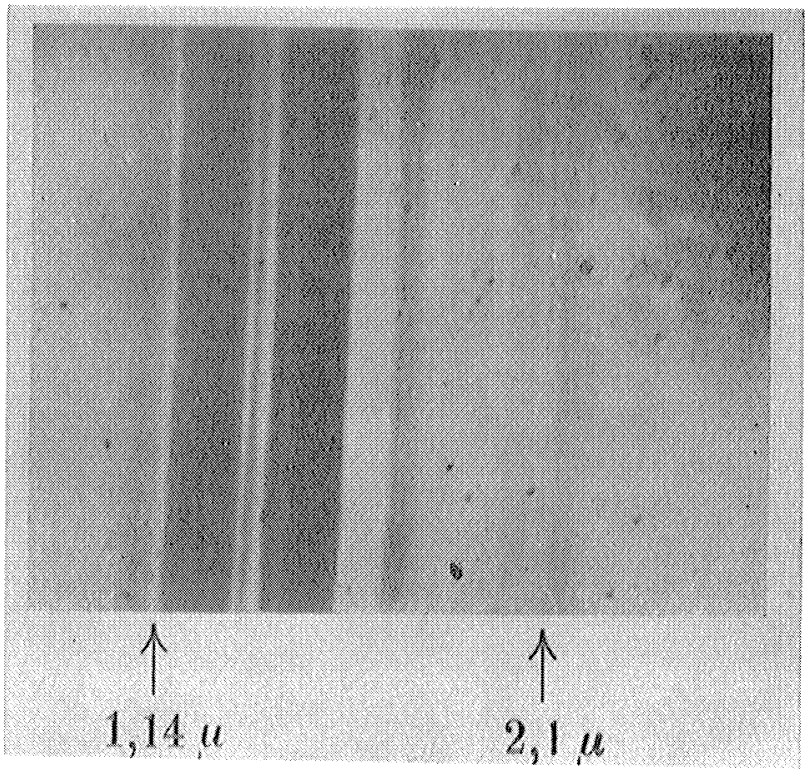

Figure 8 - Absorption spectrum of liquid methylene chloride.

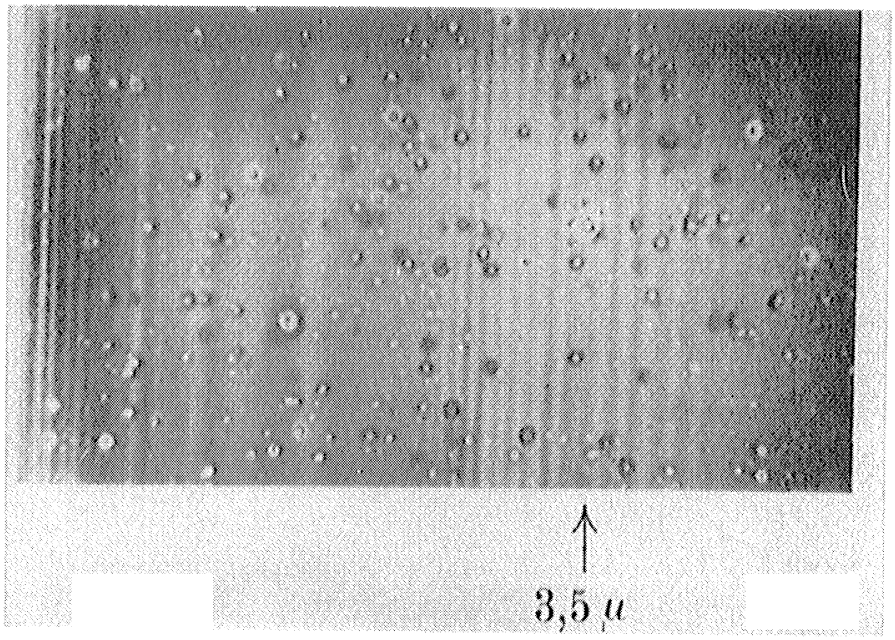

Figure 9 - Rotation-vibration band of gaseous HCL.

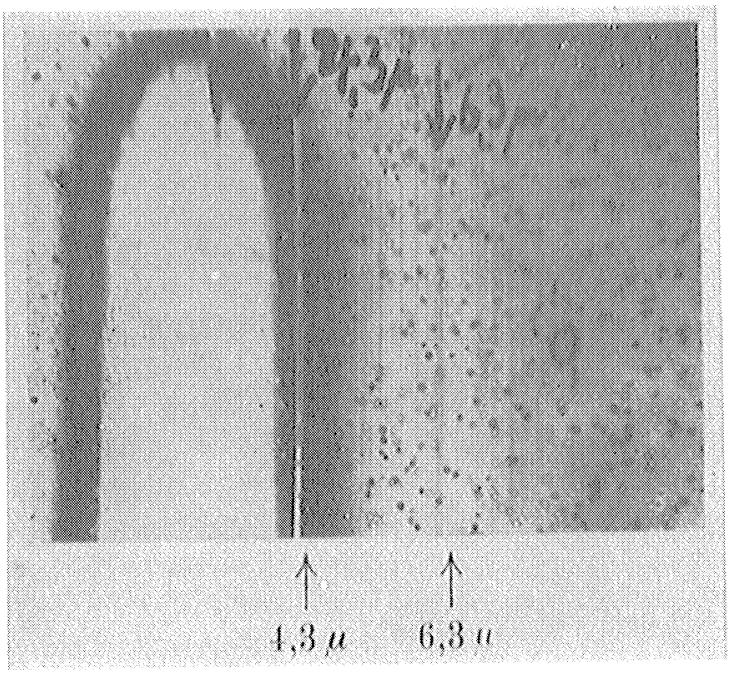

Figure 10 - Absorption spectrum of carbon dioxide and water vapor in room air.

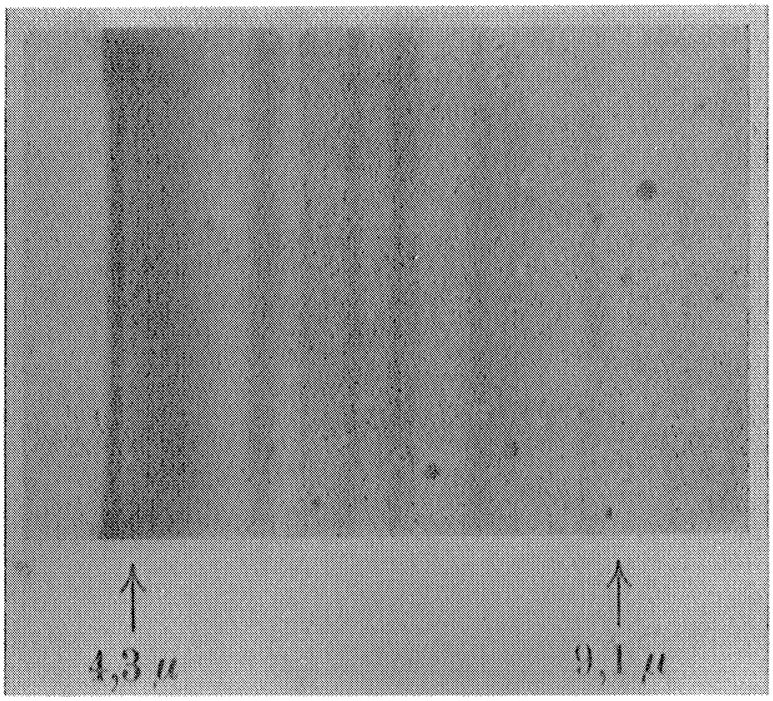

Figure 11 - Absorption spectrum of Furfurol. Opaque aluminium as the absorber.

ON THE TAKING OF PICTURES IN THE INFRARED USING THE METHOD OF CZERNY (EVAPOROGRAPH)

H. Gobrecht and W. Weiss,
Zeitschrift für Angewandte Physik 5, 207-211, 1953

Translation by M. Tribus

The (evaporograph) method first presented by Czerny in 1929 (1) and later clarified by Czerny, Willenberg, Moench, and Mollet from 1932 - 1937 (2, 3, 4) gives at present one of the best methods of taking pictures in the infrared portions of the spectrum beyond 1.2 microns wavelength. The method was examined in detail, with the aim of using the method in taking infrared spectra. The experiments which are described below serve to clarify the previous reports, so that we may now use them properly.

1. DESCRIPTION OF THE APPARATUS AND METHOD OF OPERATION

The radiation receiver consists of a thin tightly stretched film (for example, of collodion) which is coated on one side with a black layer (in our case soot). The other side is wetted with a very thin layer of liquid. The film is located in a metal frame which is held against the walls of a metal cylinder with slight pressure. The vessel is closed at one end by a plate of potassium bromide and at the other with a glass plate (see Fig. 1). The interior is at the state corresponding to saturation pressure of the saturated liquid. In the ideal case an equilibrium exists between condensation and evaporation on the inner glass surface and the membrane. This equilibrium can be disturbed by the absorption of radiation on the soot layer which causes a small temperature rise through the membrane and gives rise to a partial evaporation of the liquid film. The rate of vaporization can be increased by pumping the air out of the vessel. The reduction of the thickness of the liquid film is a measure of the energy density of the radiation absorbed on the black layer. To that extent the indication of radiation is similar to that of the bolometer or thermopile; on the other hand this has the advantage that it gives a picture and the rate of energy accumulation. [In contrast to the thermal element which measures rate of energy (power), we measure accumulated energy.] The liquid layer can be evaporated on the membrane in this way: a movable

heating coil is mounted in front of the membrane which can take up the liquid for about ten evaporations. This heating coil is mounted eccentrically on a key and can be rotated in front of or away from the supporting membrane.

Because of the thickening of the liquid film, illumination by white light will produce interference colors. Light rays of wavelength λ falling on the surface at an angle α will be entirely extinguished if the equation $2D\sqrt{n^2 - \sin^2\alpha} = k\lambda$ is satisfied ($k = 1, 2, 3\ldots$; n = index of refraction, D = film thickness). In the use of white light, there will remain only those colors which have not been cancelled and which, for the particular angle of incidence, are maximally reflected. For small angles of viewing and $n \simeq 1.4$, we have calculated the following apparent film colors for the following film thicknesses.

k = 1	yellow	0.157 micron
	red	0.193 micron
	blue	0.201 micron
	green	0.225 micron
k = 2	yellow	0.314 micron
	rose-red	0.386 micron
	green-blue	0.402 micron
	green	0.450 micron

The color contrasts give a measure of the sharpness of the picture. In visual observations the standard visibility function for the eye indicates that the contrast green-red or green-blue permits one to measure, in first order fringes, a film thickness variation on the order of 30 millimicrons. There will be improvement, therefore, if the picture is illuminated, not with white light, but with light from an incandescent lamp filtered through copper sulfate solution. This has the added advantage that the infrared radiation from the incandescent lamp will be filtered out, preventing an unwanted vaporization effect upon the film. Of course one is not limited to visual observations of the picture; one could photograph it. By the choice of particular spectroscopic plates, one could increase the contrast even further. When the picture has been produced and photographed, the remaining layer on the membrane can be evaporated off by the radiation from an incandescent lamp before producing a new one for the next exposure.

2. SUPPORTING MEMBRANE, LIQUID FILM AND CARBON LAYER

For a double layer membrane of constant thickness there are two possibilities for the strengthening of the vaporization picture: (1) Use a thin supporting membrane of no specific color. The thick layer of the vaporizing substance will show a basic color and color variations. (2) Use a thick membrane with a characteristic color. The thin film of the vaporizing substance will show variations of the basic color.

We have used both possibilities. At the present time we use the second possibility since the membrane is thus stronger and the diffusion of the liquid through the membrane to the back of the graphite is reduced. The decrease in heating with a thick membrane can be neglected on the basis that the soot layer (5 to 15 microns) is 50 times thicker than the optically flat double layer (0.2 microns). We have therefore regularly used membranes which show the characteristic color red in the first order interference under normally incident light and display green as the first order interference color upon coating with liquid. In this way, using blue illumination, we see, upon partial vaporization, a dark picture on a light background. Upon further coating with liquid (to the second order red interference) one can obtain pictures of the opposite contrast.

For the production of clean, air free membranes, we have used collodion which has been dissolved in a mixture of 50 per cent amyl-acetate and 50 per cent ether. The Lacquer Z-116 from Agfa-Wolfen, previously used by Czerny and his co-workers, is no longer available. Lately we have been obtaining good results with Aluminum oxide foils. The investigations on this matter are not yet concluded. The production of the collodion membranes is carried out in the following way: A 2.5-mm thick and 5-mm high metal ring of 50-mm diameter, which will later carry the membrane, is placed in the center of the bottom of a 30-40-cm diameter glass cylinder filled with distilled water. A few drops of the collodion solution placed upon the surface of the water quickly spreads out over the surface and forms a thin film. A half minute after the placing of the lacquer, the water is absorbed. The membrane which has been placed on the ring is removed from the trough with great care and placed to dry in a drying chamber at 50 to 60° C. It is convenient to lay a membrane which, because of interference, appears red upon another yellow colored membrane, and produce a colorless membrane of appropriate thickness thereby. It is necessary to be careful that one side of the finished

membrane is completely free of dust particles (3) and all water drops. This is the side which will later be wetted by the fluid which produces the evaporation picture. For this purpose it is necessary that the liquid completely and uniformly wet the membrane. For this reason any orientation of the collodion molecules is to be avoided so that the hydrophylic character of the collodion will not be changed. In particular, contact with water must be avoided on the surface of the membrane in question. In this connection attention is called to the excellent method of preparing thin membranes by Czerny and Mollet (4).

The other side of the membranes was lightly and uniformly coated with soot over the usual petroleum flame. Blackening with Antimony, Bismuth, or Platinum, as was done by Czerny, Moench, and Willenberg (3, 4) was, for other reasons, not possible for us.

3. THE EVAPORATION MEDIUM

In order to obtain the greatest possible sensitivity and clarity, the following requirements must be placed upon the evaporating fluid.

1. Small heat of vaporization.
2. Complete wetting of the membrane surface.
3. Chemical inertness towards glass, metal, and above all, the membrane.
4. Vapor pressure at room temperature must be between 10^{-3} to 10^{-2} Torr. (1 Torr = Torricellian unit of pressure = 1 cm Hg.).

The following table gives a list of various substances which have appeared unusable as a result of our researches.

Decyl alcohol	Non-wetting
Do decyl alcohol	Non-wetting
Tetra decyl alcohol	Non-wetting
Hexa decyl alcohol	Non-wetting
Octa decyl alcohol	Wets in solid form. The vapor pressure is too low.

Glycerin	Non-wetting. Instead builds up in fine drops without interference colors. Does not come off when heated radiantly. In about 5 minutes the membrane begins to swell.
Benzyl alcohol	Swells and dissolves the membrane
Cinnamic aldehyde	Dissolves the membrane
Anisaldehyde	Swells and dissolves the membrane
Phthalic acid di-ethyl ester	Dissolves the membrane
Glycerin Triacetate	Dissolves the membrane
Citronella	Swells the membrane
Acetophenone	Dissolves the membrane
Oxyacetophenone	Dissolves the membrane
Cyclohexanone	Does not wet the membrane
Nitrobenzene	Does not wet the membrane
2-Methyl aniline	Swells the membrane
Monomethylnaphthalene	Does not wet the membrane

Hexadecane[1] is the only substance used, even though this paraffin has the disadvantage that it loosens stopcocks, wax seals and connections. On the other hand, this substance has the advantage, as noted by Czerny and his co-workers, that even for long exposure times the image barely becomes grainy. One can see very clearly, on the basis of these investigations, that many more substances could be used if the membrane did not swell or dissolve. For this reason we have experimented, with good results, with aluminum oxide foils, concerning which we will report later.

[1]"Pure Hexadecane" has been courteously donated to us by the Max Plank Institute for Coal Technology, Mulheim, Ruhr.

4. THE SPONTANEOUS EVAPORATION OF THE LIQUID FILM FROM THE MEMBRANE

Even in the absence of direct radiation there occurs a free vaporization of the liquid layer from the membrane in a period of a few minutes. For this reason the exposure time and therefore the sensitivity of the method are greatly reduced. Further, the sensitivity is no longer only dependent upon the previously considered rate of oil film thinning $(dD/dt)_s$, caused by the radiation, but rather the difference between this diminution and the spontaneous diminution $(dD/dt)_o$ in accordance with

$$\epsilon = \left(\frac{dD}{dt}\right)_s - \left(\frac{dD}{dt}\right)_o .$$

Since both terms increase with diminishing air pressure, there is an air pressure such that the thickness difference $\epsilon\Delta t$ during the exposure time Δt will be large enough and remain long enough to be photographed. It is not expedient to obtain larger Δt for the same $\epsilon\Delta t$, to raise the air pressure. Further, in the use of more rapidly vaporizing materials, for example, tetradecane, the decrease in the air pressure has no effect since the time to photograph the pictures is too short.

In our researches with Hexadecane we have worked with 20° C. room temperature and air pressure of 10^{-3} Torr. (10^{-2} mm Hg) with maximum exposure time Δt = 5 minutes. The picture remained for the same time. The photographing of the picture required approximately 30 seconds using Perutz-Perulith Film at a relative aperture of f/6.3. To diminish the spontaneous evaporation we have wetted the container walls with hexadecane.

Willenberg and Moench cited impurity of the evaporating substance as a cause for spontaneous vaporization (2, 3, 4). Since we had good reasons for rejecting this hypothesis, there remained for us only the possibility that the free evaporation was caused by undesirable radiation fluxes. The free vaporization could occur as a result of a non equilibrium vapor pressure if the soot surface were warmer than its surroundings. In one case a membrane, one side of which was partially blackened and the other side of which was entirely coated with oil, showed an uneven film ten minutes after the pump was disconnected. The liquid layer over the area

not soot-coated showed a tenfold greater thickness. Not until one hour after the disconnection of the pump did the thicknesses of the oil over the surface equalize. Radiation was thus indicated. At first it was felt that the different behavior of the sooted and unsooted halves of the membrane could be expained on the basis of different over-all heat capacitance. But then it would not be easy to explain why after some time and after continued vaporization the retention (of oil) differs, even though the vaporization is taking place from both halves during the same time. Finally, if the explanation is to be based on different heat capacitance, different condensation rates should be observed, but they have not been found. This study furthermore excludes the possibility that a variation in absorptivity could cause a variation in (localized) evaporation rates.

5. A FEW EXAMPLES

Figure 2 shows an example of a photograph of a spectrum. It shows the emission spectrum of a high pressure mercury arc between 1 and 2 microns and a calibration scale superposed. Figure 3 shows the absorption spectrum of Erbium glass, contaminated with Samarium and Dysprosium. Unfortunately only a small glass spectrograph was available for our photographs.

Figures 4 to 7 show photographs (taken) by thermal rays. The pictures were made with a front-surface silvered concave mirror of 35-cm focal length and 7.5-cm aperture. The distance from the object to the mirror was approximately 3-4 meters. The room temperature was 20° C. Figure 4 is a 3/4 filled coffee cup at 70° C. Figure 5 is the same at 38° C. Figure 6 is an evaporograph of a man's hand with a skin temperature of 32° C. and Figure 7 is a man's profile. The exposure time for the pictures required 1/2 to 1 minute. We shall in the next paragraph use the photo of the hand to give a calculation of the practical sensitivity of the method as revealed by our researches. Also, the appearance of the contrast variations which occur at the edges of the picture of the warm body (as in the coffee cup) as previously discussed by Willenberg (2) will be considered.

6. SENSITIVITY, RESOLUTION AND EFFICIENCY

The photo of the hand serves as an example of the maximum efficiency of our apparatus. If the radiations from the hand approximate those from

a black body at 32° C, in the room temperature of $T_o = 293^o$ K, the power density from the hand, relative to the surroundings is

$$B = \sigma \left[T_o^4 - (T_o + 12)^4\right] = -7.5 \times 10^4 \quad \frac{\text{ergs}}{\text{sec cm}^2} \cdot$$

In the ideal case, on the picture surface, with the hand located at S = 400 cm from the concave mirror, with the mirror diameter, $\phi = 7.5$ cm, the focal length f = 35 cm, and the membrane 3 cm^2, the power density on the membrane is:

$$B = \frac{B\pi\phi^2}{4s^2} \left(1 - \frac{s}{f}\right)^2 = 2.2 \times 10^3 \quad \frac{\text{ergs}}{\text{cm}^2 \text{ sec}} \cdot$$

Our studies show this is sufficient to register in one minute. Since we can use exposures up to a maximum of 5 minutes, one can detect 4.4×10^2 ergs/sec cm^2 on a 3 cm^2 surface. Furthermore, this intensity does not occur on 3 cm^2 but on a tiny area which may span only 100 microns (see below) or 10^{-4} cm^2. On this surface there falls only about 10^{-2} ergs/second or 10^{-9} watts can be detected.

One can, in a simplified way, obtain a survey of the properties of the oil, and especially the dependency on an admixture of an inert gas (air), as they affect the evaporation or absorption. Under the very great simplifying assumption that the vapor at the surface of a liquid where a temperature rise ΔT is produced has its saturation pressure p_s even in the presence of a contaminant gas at pressure p_L, and the further assumption that the reduction in evaporation or condensation velocity depends on the ratio of the mean free paths $[\lambda_{Ls}/\lambda_s]$ to a power x, wherein λ_s is the mean free path in the saturated vapor and λ_{Ls} that in the vapor with its contaminant gas, we may obtain, using:

$$\lambda_s = \frac{RT}{\sqrt{2}\,\pi\sigma_s^2 N_L p_s} \qquad \lambda_{Ls} = \frac{RT}{\pi N_L \left[p_s \sigma_s^2 \sqrt{2} + p_L \sigma_s^2 \sqrt{1 + M_s/M_L}\right]},$$

the number of vapor molecules per second which strike one cm^2 of the surface and which have an accommodation coefficient a and heat vaporization $\Lambda = \Lambda(T., \ldots)$,

$$\dot{Z} = \frac{a p_s}{\sqrt{2\pi M_s R^3 T^5}} \left[\frac{1}{1 + a \frac{p_L}{p_s}} \right]^x N_L \Lambda \Delta T \ ,$$

Where:

R = gas constant,

M = molecular weight,

$$a = \frac{1}{2} \sqrt{2} \left(\frac{\sigma_{Ls}}{\sigma_s} \right)^2 \sqrt{1 + \frac{Ms}{M_L}} \ ,$$

σ = particle radius,

$$\sigma_{Ls}^2 = \sigma_L^2 + \sigma_s^2 \ ,$$

N_L = Loschmidt No. (no. molecules/cm^3 at S. C. T. P.).

From this there results, with ρ_{fl} = density of the oil liquid, a thickness variation during irradiation time Δt,

$$\frac{dD}{dt} \Delta t = \frac{a \Lambda p_s \sqrt{\frac{M_s}{2\pi R^3 T^5}}}{\rho_{fL} \left[1 + a \frac{p_L}{p_s} \right]^x} \Delta T \ \Delta t \ .$$

This then shows that the rate of thickness variation is independent of the value of p_L for $p_L \ll p_s$.

A measure of the dependence of radiation time needed to vaporize a given thickness of fluid per cm^2 (for example to vaporize a hexadecane mass, Δm), upon the air pressure is given in Figure 8. The energy density utilized is for Curve I, 10^4, and for Curve II, 2.5×10^3 ergs/sec cm^2. Δm in both cases is 3×10^{-6} g (the color change corresponding to $\Delta D = 0.04$ microns). The flux of energy was produced by a burning candle, measured with a thermopile and varied through the use of a diaphragm. The air pressure was indicated by a McLeod type manometer. By more accurate measurement it is possible with this method of observing color changes to obtain useful information on the absorptivity of different liquids on foreign surfaces.

The most important thing for this method, of course, is that the exposure time Δt necessary to generate a given thickness variation per cm^2 should be inversely proportional to the energy density, B, in the radiation. That this requirement is very well fulfilled has been shown by Czerny and Mollet (4). Our further measurements are given in Figure 9. In this figure the ordinate is the reciprocal of the square of the aperture, ϕ, in cm^{-2}, to which the energy density is inversely proportional. At $\phi^{-2} = 0.5\ cm^{-2}$, $B = 8 \times 10^4$ ergs/sec cm^2 (as measured by a thermopile). Further $\Delta m = 3 \times 10^{-6}$g. The air pressure, p_L, and soot layer thickness, d_R, were used as parameters. The latter was determined approximately by weighing. Larger values of d_R not only increase the absorptivity but also, due to lateral heat conduction in the layer, reduce the sharpness of the picture. We found by taking pictures of a calibrated test chart that when $d_R = 8$ microns, lines spaced more than 60 microns apart could be resolved. For $d_R = 15$ microns, the spacing must exceed 120 microns.

Using a thinner membrane which had been oiled (by diffusion of the contaminating oil) and had heavier graphite particles, $d_R = 5$ microns and lines more than 80 microns apart could be resolved.

Czerny, Mollet and Willenberg (2, 4) reached similar values.

Theoretically this variation in resolution which we have noted should increase with the ratio:

$$q = \frac{\text{heat conduction through the film}}{\text{heat conduction laterally in the film}} .$$

The calculation for an irradiated disk of radius r, gives

$$q = \frac{r}{2d_r}$$

q is therefore smaller if one considers only a narrow spectral line instead of continuous thermal radiation.

By the above calculation the practical sensitivity of the evaporograph is only about one or two orders of magnitude smaller than that of the thermopile, although the latter has a much smaller efficiency than the evaporograph. The thermopile is, according to Czerny, a heat machine with the thermodynamic efficiency $\eta = \frac{\Delta T}{T}$, where ΔT is the well known temperature rise through heating and T is the surrounding temperature. In the evaporograph, however, this temperature rise is extraordinarily small. Therefore it appears that the efficiency of the evaporograph does not rest on a thermodynamic basis but must be explained on the basis of elementary processes, therefore by the direct transformation of radiant energy into kinetic. An expression for the macroscopic efficiency of the apparatus can be obtained from the quotient:

$$\eta = \frac{\text{The energy } E_V \text{ required to vaporize a given oil mass as needed to give pictorial representation}}{\text{The input energy during the vaporization process, E.}}$$

η may be computed approximately from the following example: Using an irradiation of 10^4 ergs/cm^2, an oil mass of 3×10^{-6} g/sec evaporates in 1.5 seconds. The heat of vaporization of hexadecane is approximately 50 cal/gram. From this the effective efficiency is 50 per cent, very high. Losses occur because of reradiation by the absorbing layer (E_s) and heat conduction in the layer (E_L). Because of these one has

$$\eta = 1 - \frac{E_L + E_s}{E} .$$

Czerny (1) has calculated that E_S and E_L are in order of magnitude 100 times smaller than E_V. In view of this high efficiency there would be no limit to the sensitivity of the method if the spontaneous vaporization could be reduced.

SUMMARY

A newly assembled apparatus has been described and the behavior of different vaporizing materials has been investigated. Basic considerations of the limit of the sensitivity show that the spontaneous vaporization of the liquid layer lowers the attainable sensitivity. On the basis of the experimental measurements a sensitivity of 10^{-9} watts of radiation has been reached.

REFERENCES

Number	Title
1	Czerny, M., Zeit. f. Phys. 53, 1 (1929)
2	Willenberg, H., Zeit. f. Phys. 74, 663 (1932)
3	Moench, G. and Willenberg, H., Zeit. f. Phys. 77, 170 (1932)
4	Czerny, M. and Mollet, P., Zeit. f. Phys. 108, 85 (1937)

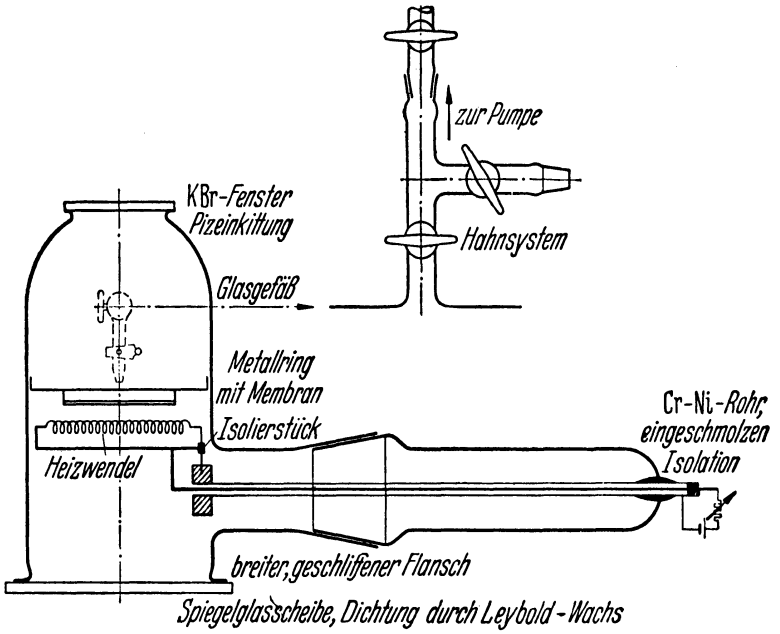

Fig. 1. The radiation receiver (Semi-schematic)

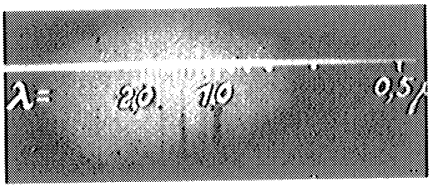

Fig. 2 Spectrum of a high pressure H_g lamp.

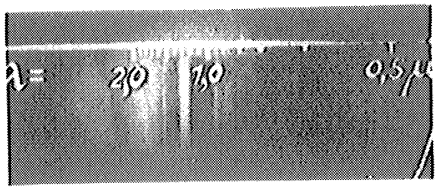

Fig. 3 Absorption Spectrun of a Sm - Dy - Er Glass

Fig. 4 Picture of a warm coffee cup at 70^{o} C, self-radiation.

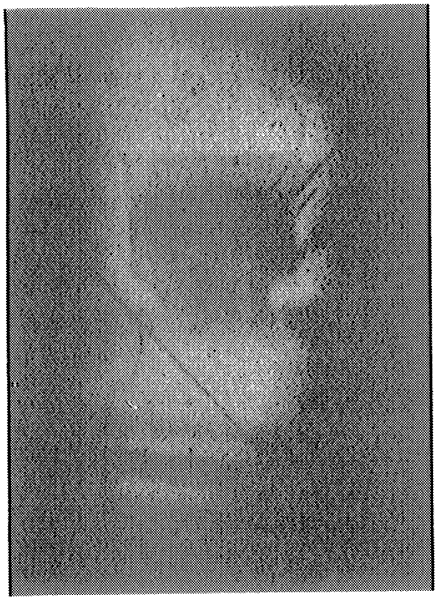

Fig. 5 Picture of a warm coffee cup at 38^{o} C, self-radiation.

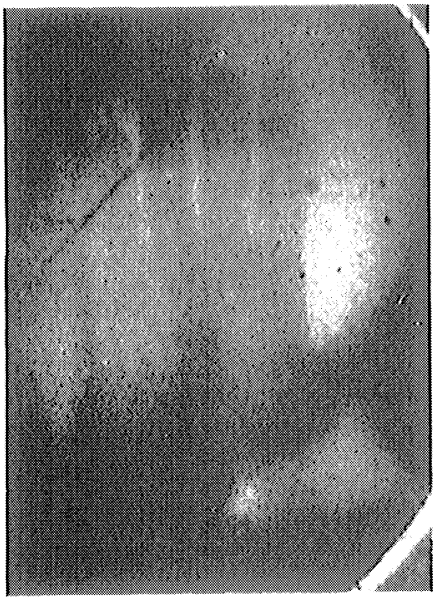

Fig. 6 Picture of a man's hand, self-radiation.

Fig. 7 Picture of a man's profile, self-radiation.

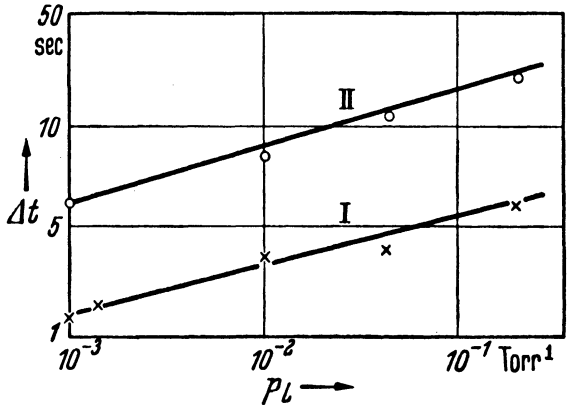

Fig. 8. The irradiation time required to vaporize 3×10^{-6} grams of hexadecane as a function of the air pressure in the container.

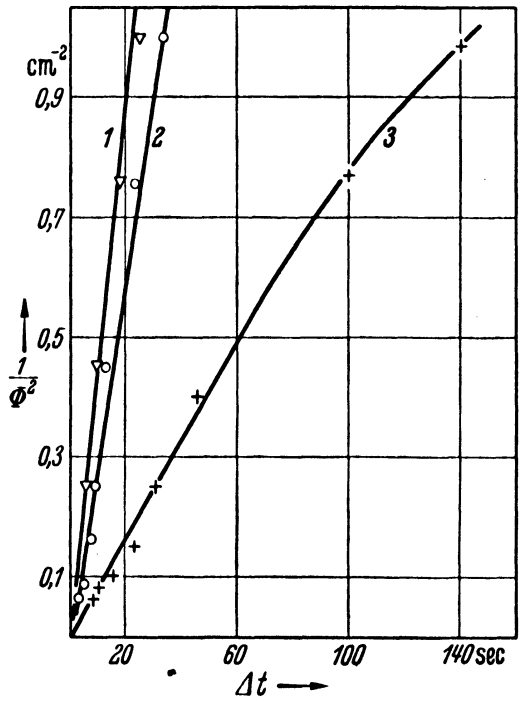

Fig. 9. Demonstration that the quantity $\phi^2 \Delta t$ = constant for

1. Air pressure = 10^{-2} mm Hg, d_R = 15 microns
2. Air pressure = 10^{-2} mm Hg, d_R = 8 microns
3. Air pressure = 5 mm Hg, d_R = 8 microns

[1] 1 Torr = 1 mm Hg pressure.

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