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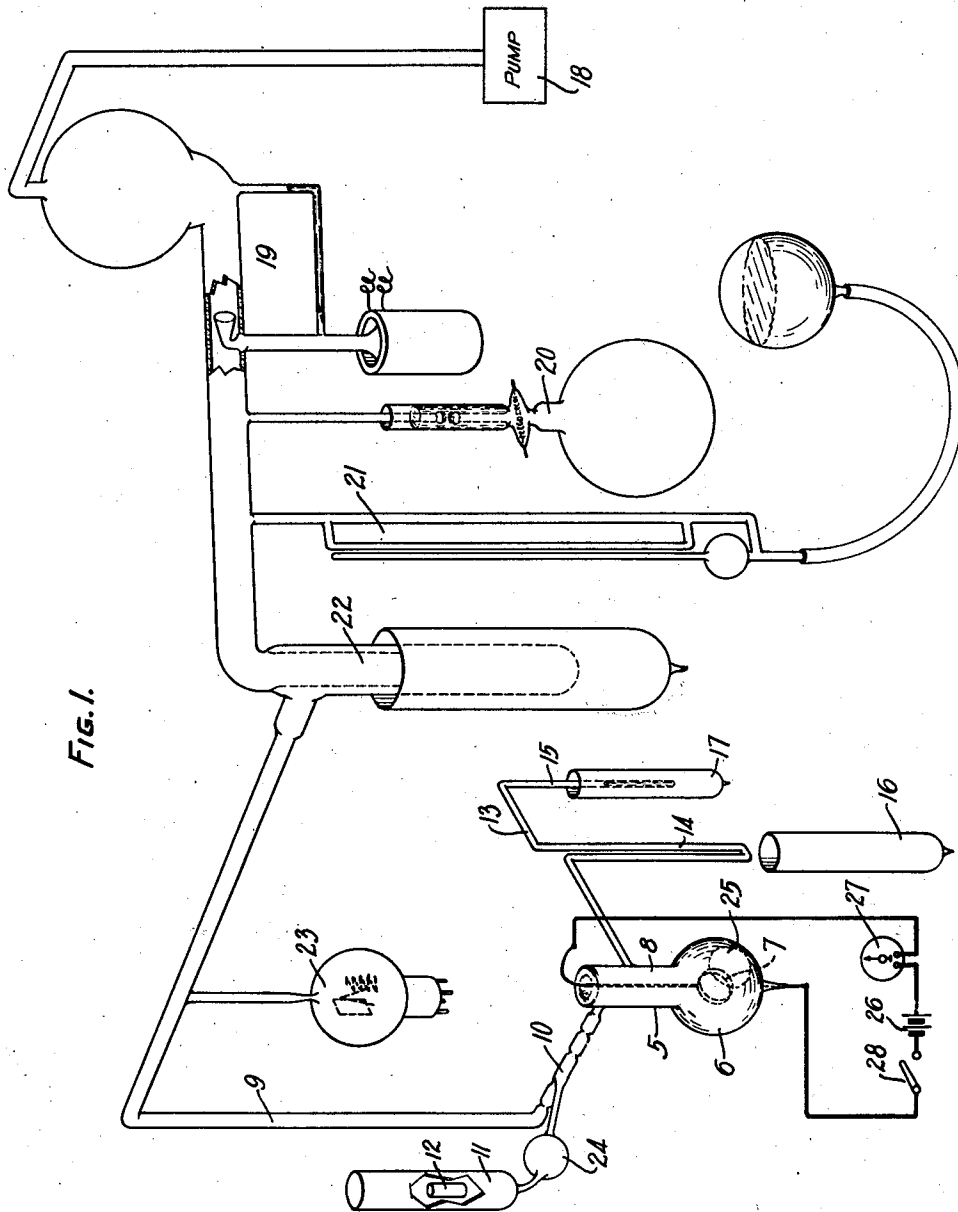
A. R. OLPIN

2,008,874

PHOTO ELECTRIC TUBE

Filed April 6, 1929

8 Sheets-Sheet 1



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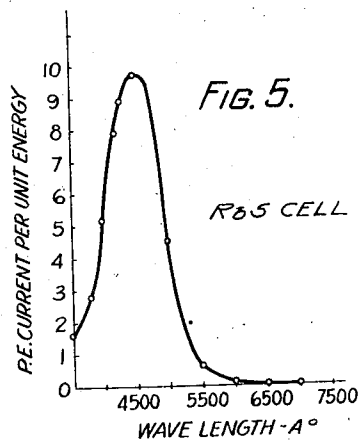
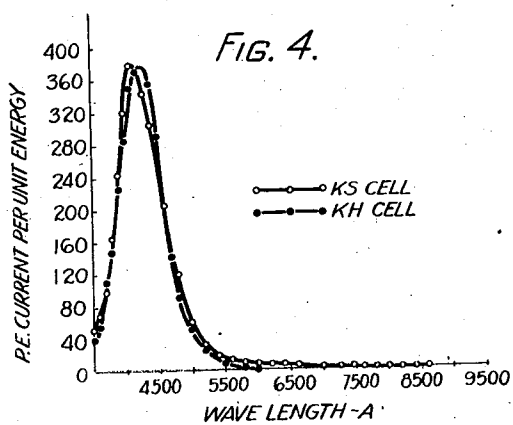
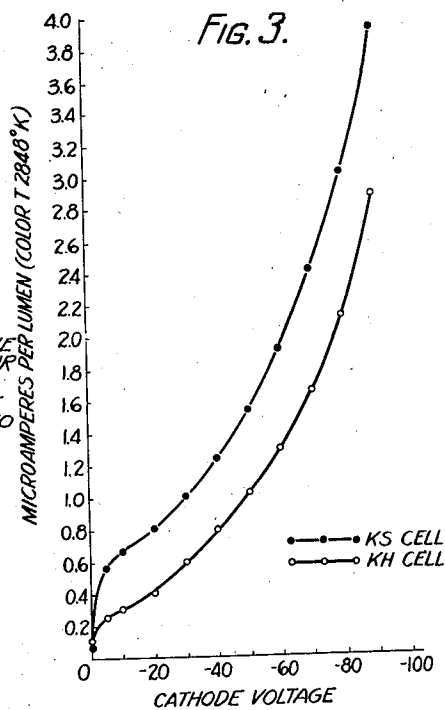
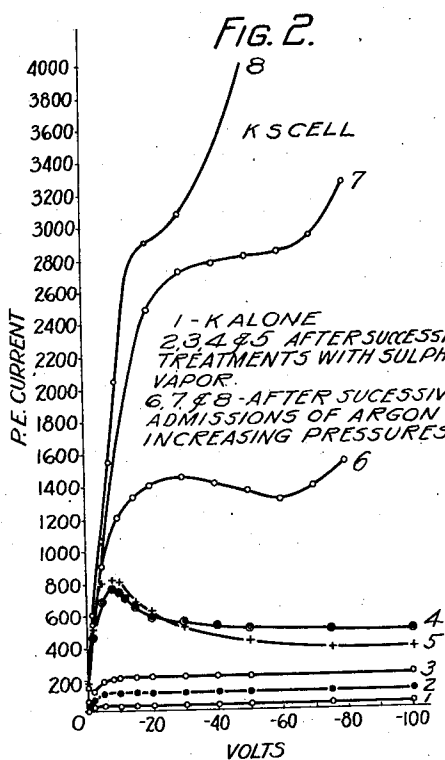
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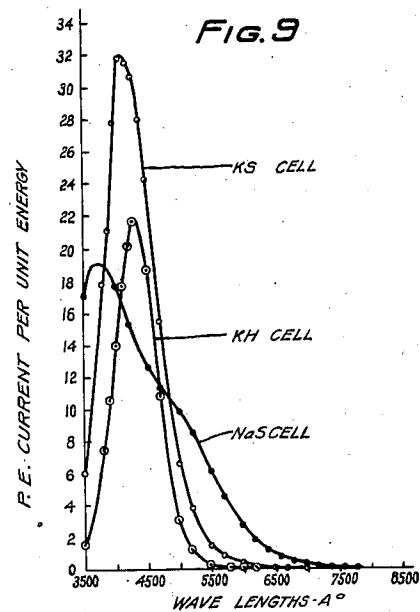
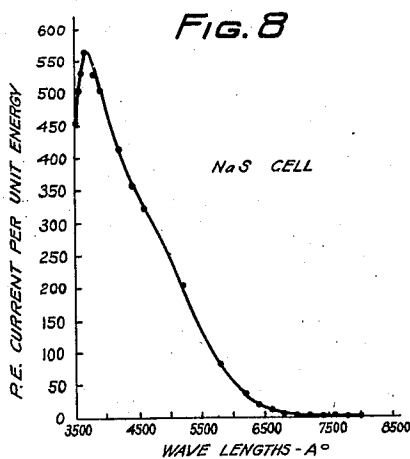
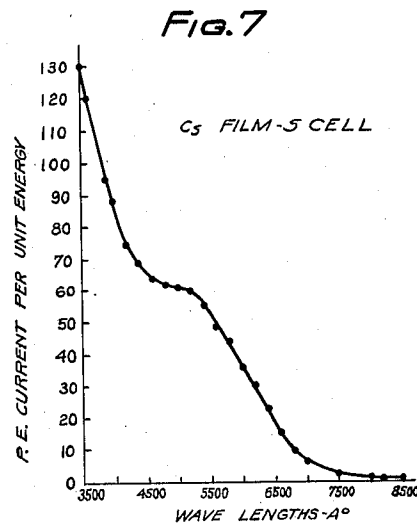
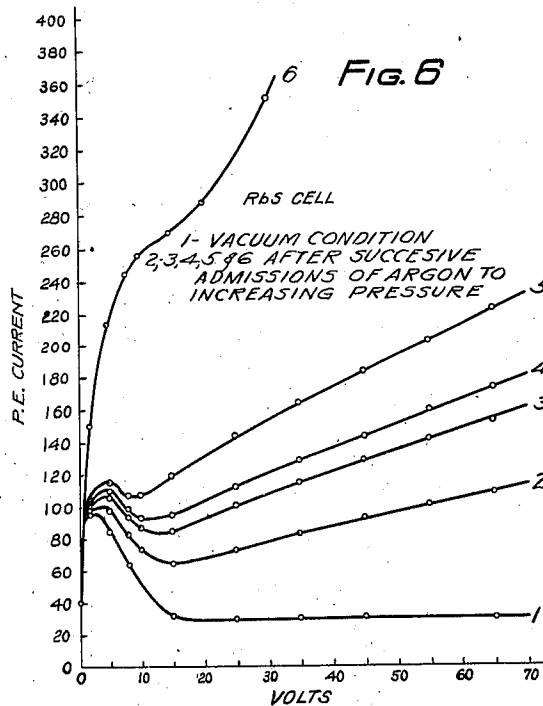
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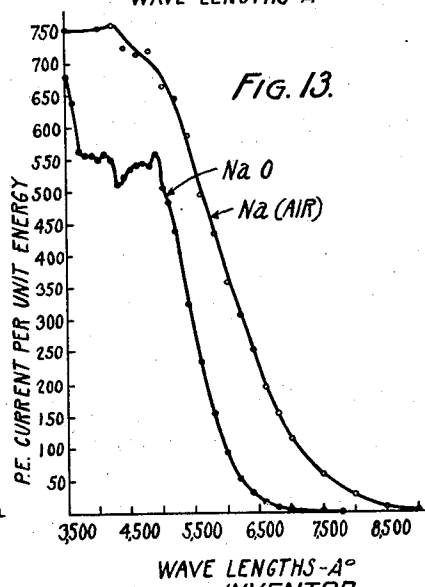
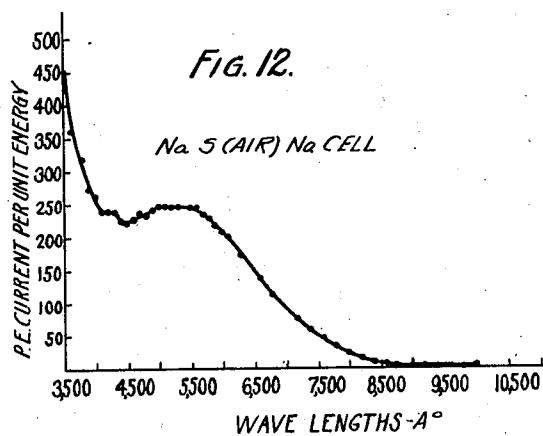
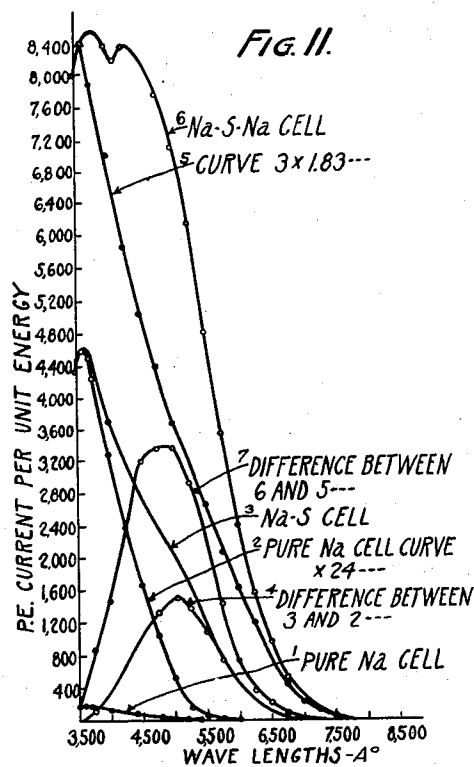
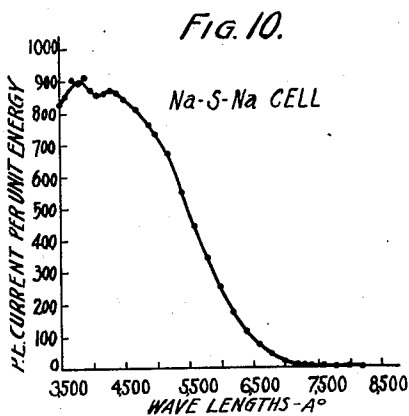
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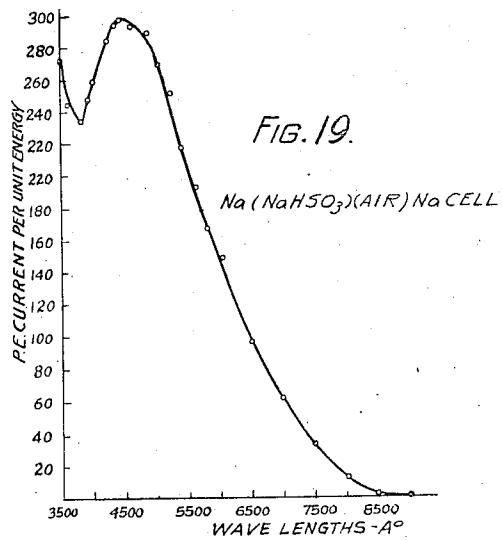
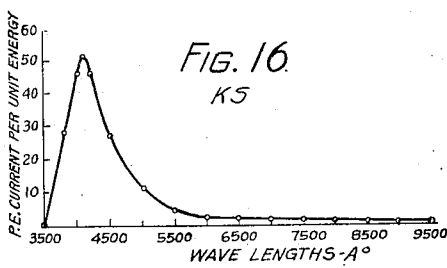
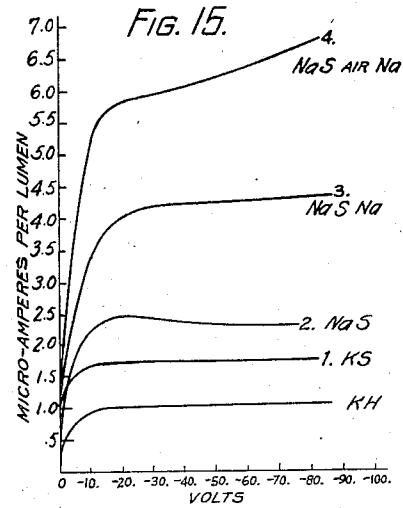
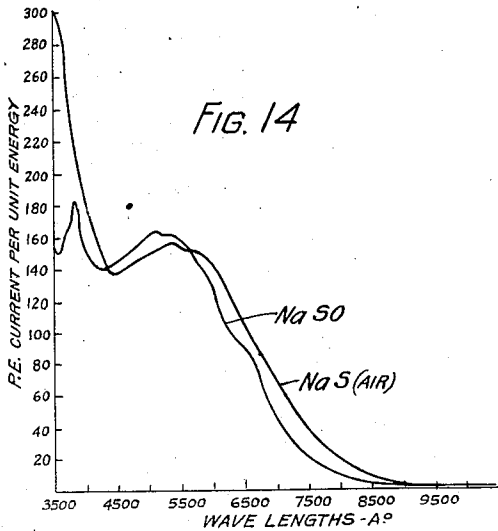
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FIG. 18.

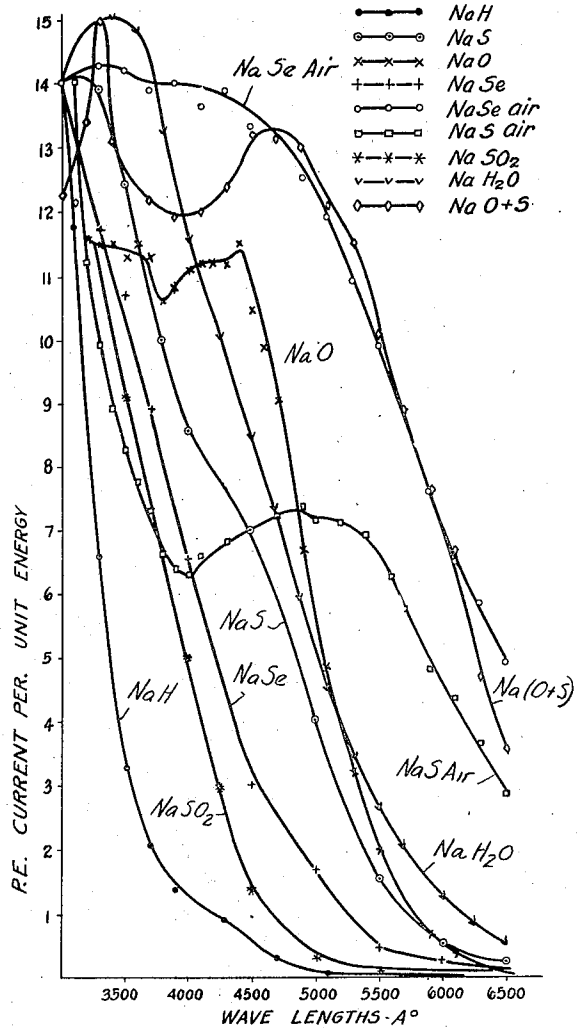
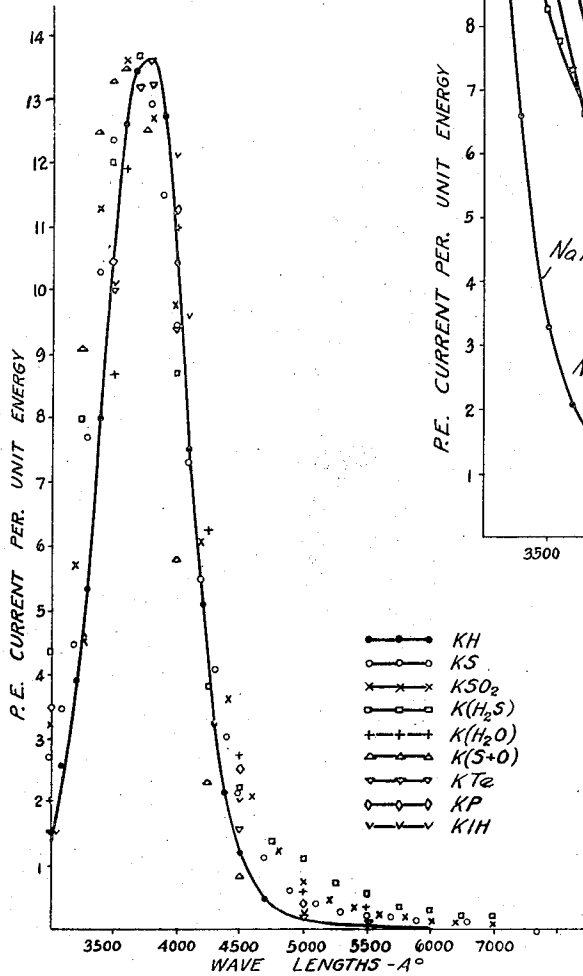


FIG. 17.



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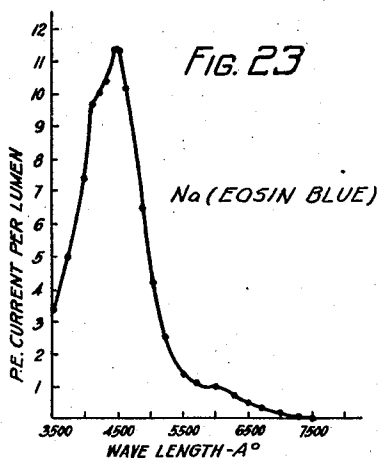
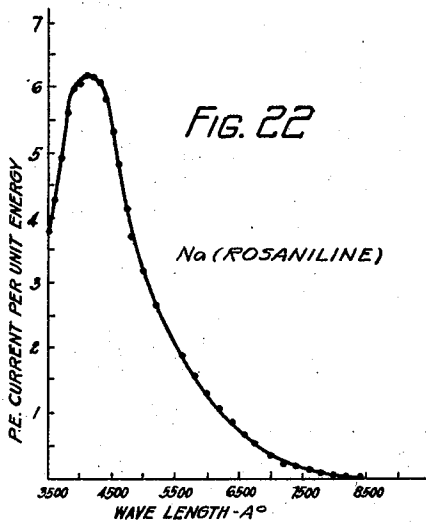
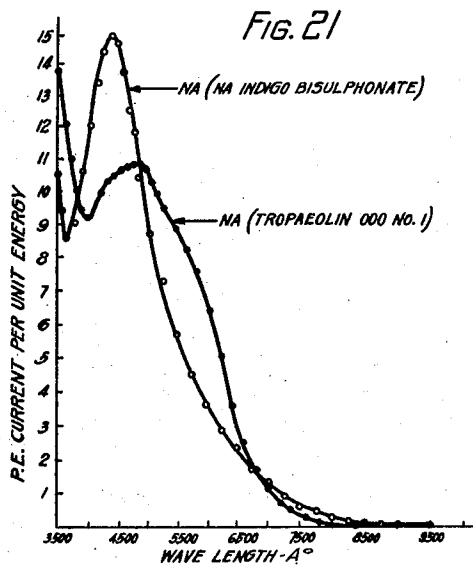
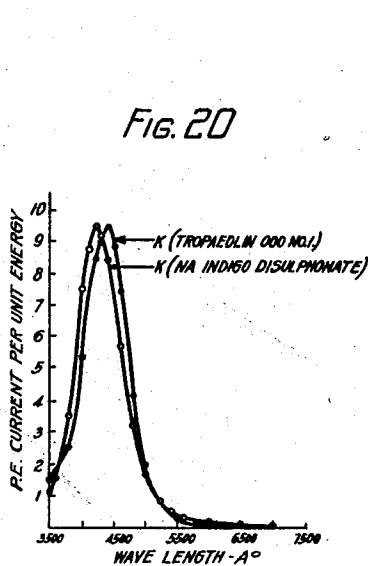
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8 Sheets-Sheet 7



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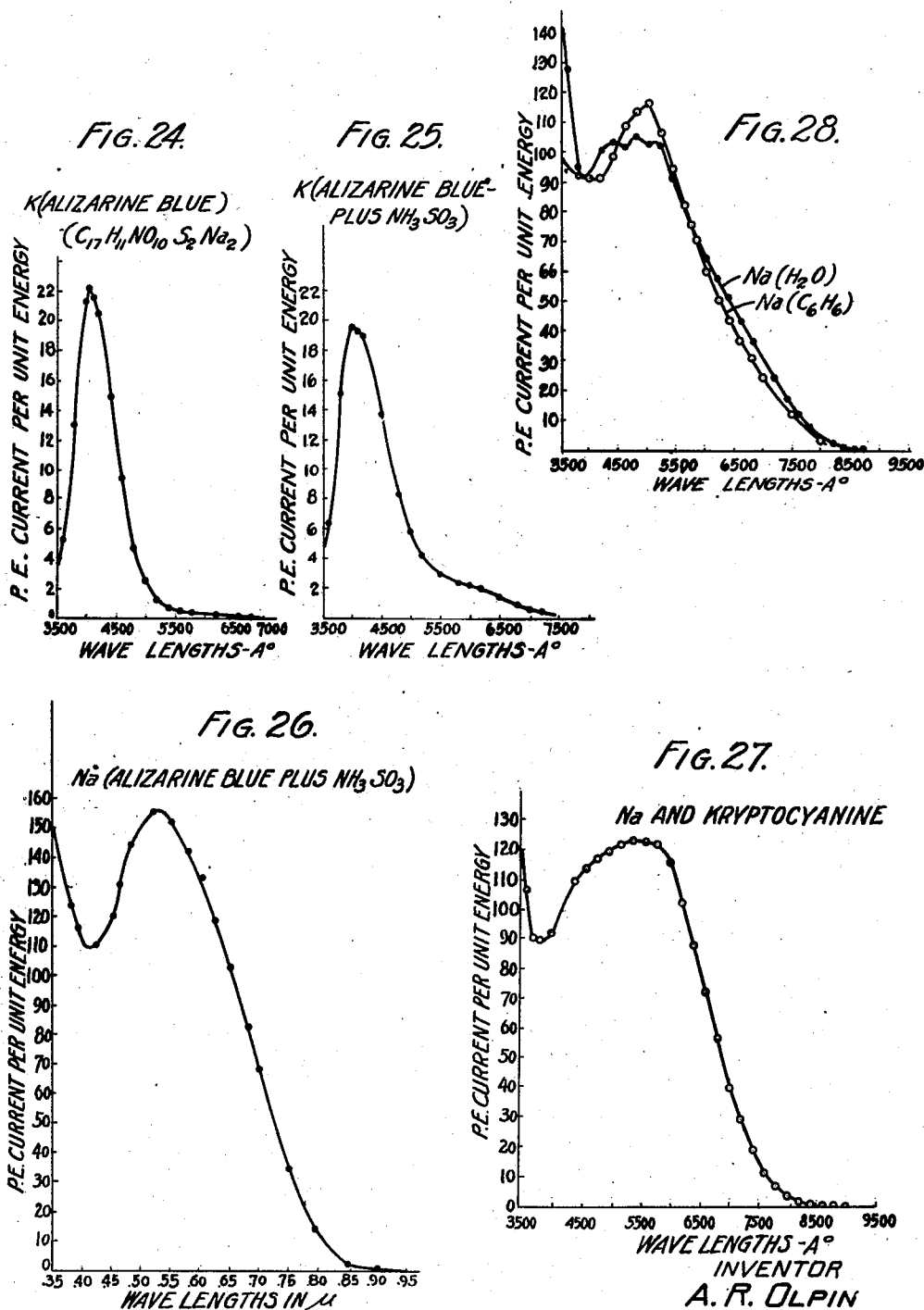
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8 Sheets-Sheet 8



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UNITED STATES PATENT OFFICE

2,008,874

PHOTO-ELECTRIC TUBE

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Application April 6, 1929, Serial No. 353,176

13 Claims. (Cl. 250—27.5)

This invention relates to optics and electro-optics and particularly to light-sensitive electric devices and methods of making them.

5 An object of the invention is to increase the sensitivity of photoelectric tubes.

Another object of the invention is to increase the sensitivity of photoelectric tubes to red light.

Other objects and advantages will be apparent from the description which follows.

10 Many attempts have heretofore been made to improve the sensitiveness of photoelectric tubes to light rays within the so-called visible spectrum and particularly to red rays. As is well known, the potassium-hydride tube, which has been very generally used for many years, is most sensitive to blue light and responds very little to red light. Moreover, its sensitiveness even to blue light is so small that the photoelectric current has to be given enormous amplification for most purposes.

15 In accordance with the present invention photoelectric tubes are provided which have an increased maximum sensitivity which may be made to be many times that of tubes heretofore used and which are highly sensitive to red light. Moreover, it has been discovered that sensitiveness to red light may be obtained in a tube employing light sensitive material which is not sensitive to such light by associating with the light sensitive material another substance which is capable of modulating the red light with a resonance frequency of its own to produce modulation frequencies such as a side frequency (sum or difference frequency), to which the photoelectric material employed is highly sensitive. Incident red rays therefore may produce a large photoelectric current even when the photoelectric material employed is not at all sensitive to such rays. Thus, for example, a layer of sodium may be employed as the light sensitive substance and be covered with a thin layer of dielectric material obtained by heating flowers of sulphur (which may contain traces of water) in a side tube connected to the tube and exposing the sodium surface in vacuo to the substance given off. There is thus formed upon the sodium surface a thin layer of dielectric which is capable of modulating incident red light by a resonance frequency of its own in the infra-red to produce a modulation frequency in the region to which sodium is particularly sensitive. Such a tube

may be further greatly improved by methods herein described.

Many materials suitable for use with a so-called light sensitive material to modulate incident light and so shift the effective frequency to a desired position are mentioned in this specification. In accordance with the invention any of these materials or combinations of them or other materials having the same property may be used for modulating, not only in photoelectric tubes, but in other devices where a change of frequency may be utilized to advantage.

A more detailed description of the invention will now be given having reference to the accompanying drawings.

Fig. 1 shows schematically a layout of the apparatus used in making photoelectric tubes according to this invention.

Figs. 2 to 28 are curves showing characteristics of cells made up according to this invention.

Referring to Fig. 1, the apparatus used in making photoelectric tubes according to this invention will now be described. The tube proper comprises a glass vessel 5 having a substantially spherical-shaped portion 6 which is about two inches in diameter. The cathode of the tube is formed on the inner surface of the portion 6. An anode 7 in the form of a nickel ring is supported from the stem 8. The vessel 5 is connected to a vacuum pump station by a glass tube 9. Between the tube 9 and the vessel 5 is a distilling tube 10 to which is connected a side tube 11 within which photoelectric material within a glass capsule 12 is placed prior to being distilled into the vessel 5. A tubulation 13 comprising a U-shaped portion 14 and a sealed end-tube 15 is also sealed to the stem 8 of tube 5 through which the various dielectric materials employed according to this invention are introduced. Dewar flasks 16 and 17 are provided for cooling the U-tube 14 and the dielectric tube 15, respectively.

The vacuum pump station comprises a vacuum pump 18, a mercury vapor pump 19, an arrangement 20 for introducing inert gas, a McLeod pressure gauge 21, a liquid air trap 22 and an ionization gauge 23.

The cathode of one tube to be described by way of example comprises an opaque layer of

potassium, the surface of which is treated with the gaseous material evolved from flowers of sulphur when heated. A capsule 12 of previously purified potassium is inserted in the chamber 11 which is then sealed. The flowers of sulphur are placed in the tube 15 which is then sealed to the tubulation 13. The chamber 11 and the capsule 12 are then heated until the potassium within the capsule 12 is sufficiently molten to break through the end crust of oxide and flow into the bulb 24. The chamber 11 is then sealed off from the bulb 24. From the bulb 24 the potassium is successively distilled through the bulbs of the distilling tube 10 to form an opaque layer of potassium on the inside of the spherical member 6. Prior to the formation of this layer of potassium the system is thoroughly evacuated and the vessel 5 outgassed by heating. By means of a point flame a window 25 about one inch in diameter is made on one side of the bulb 6 through which to introduce the exciting light. After the potassium coating has been formed the side tube 15 is heated until the sulphur melts. Surprisingly little gas is given off during this heating, the manometer reading on gauge 21 being scarcely detectable. During the time that the sulphur is being heated, a test circuit comprising battery 26 and galvanometer 27 is completed by the closing of switch 28 in order that any change in response to light may be noted readily. The pump is left running during the treatment of the surface. The sulphur sublimes easily with little additional heating, so that it is easy to control the amount entering the photoelectric cell 5. Light from a constant source is directed normally through the window onto the back of the tube. The amount of dielectric introduced is determined by the sensitivity conditions desired.

Table 1 gives a typical history of the process of sensitizing a potassium surface and the relative current values for two different polarizing voltages at every stage in the making.

Table 1

Cathode history	P. E. current at cathode voltages	
	-8 Volts	-50 Volts
	Units	Units
Freshly distilled potassium.....	34	38
Very slight amount of sulphur sublimed in tube; no change in surface color.....	58	62
Slightly more sulphur vapor on surface.....	113	141
More sulphur vapor; no coloration of surface.....	179	217
More sulphur vapor; faint rose color appears.....	545	483
Pumped 10 minutes.....	815	380
Light passed through diffusing glass into cell.....	542	542
Pumped another 10 minutes.....	905	424
Slightly more sulphur (surface color changes to golden).....	840	386
Sulphur tube sealed off.....	846	418
Very low pressure of argon.....	1,360	2,280
Argon pressure increased to .1 mm.....	1,470	4,120

It will be noted that once the dielectric film begins to build up, as shown by a change in the surface color, the current values were larger at low voltages than at high. This has been quite generally observed with this type of tube, the voltage versus current curves showing a maximum sometimes at cathode voltages as low as -5 volts. When argon was admitted at low pressures, however, the gas curves increased from this maximum. A typical series of these voltage-current curves for a potassium surface treated with sulphur vapor is shown in Fig. 2. Since the

irregularities they exhibit could be ironed out by focusing the light on the side of the tube, or by shining it through a ground glass, they appeared to be due to directional effects caused by the geometry of the tube.

The photoelectric emissions from potassium surfaces treated as described above were not only bigger than those of potassium hydride tubes but the response to red light was decidedly larger. Even better results were obtained in some cases by flashing hydrogen on the surface. Table 2 illustrates the relative sensitivities to colored light on a scale making the emissions under action of total light equal.

Table 2

Color of exciting light	EK filter used	KSII tube	KS tube	KH tube
White.....	None	374	374	374
Violet.....	#76	11	11	20
Blue.....	#78	93	101	132
Green.....	#60	59	85	44
Yellow.....	#16	120	72	9
Red.....	#29	58	11	1

The filters used and designated by the symbol EK were standard filters made by the Eastman Kodak Company. The color temperature of the constant light source used for this table was not known but Fig. 3 shows the relative sensitivities of KS and KH cells to white light of color temperature 2848° K. The new tubes are very stable and show little change in emission upon aging, the tendency being rather to increase in sensitivity during the first few days after sealing them off the pump. In Fig. 4 are plotted some curves showing relative sensitivities throughout the spectrum. These curves taken with spectrally resolved light are corrected so that the ordinates representing current per unit of light energy incident on the surface, are equal at the selective maxima.

It will be noted that the large selective maxima for these curves lie in the same spectral region but that the maximum for this potassium sulphur cell is slightly displaced toward shorter wave lengths. The long end of the curve for the cells can be represented as an amplified sensitivity curve for pure potassium plus an additional curve representing a new maximum symmetrically drawn about 6000 Å°. The importance of this second maximum should not be overlooked. It falls in that portion of the spectrum where the energy content of radiations from most illuminating systems is large, and its presence figures strongly in increasing the response of a tube to light.

Tubes having a cathode comprising rubidium treated with sulphur vapor in the manner hereinbefore described for tubes employing potassium have also been made. Fig. 5 shows the spectral distribution relationship between wave length and photoelectric current for this type of photoelectric tube. The selective peak appears at a slightly shorter wave length after treatment than before and no second maximum in the red appears.

The voltage vs. current curve shown in Fig. 6 is unique in that the current reaches its maximum value with not more than minus three volts on the cathode rapidly decreasing to a constant value from about minus twenty volts up. The admission of argon at low pressure into the tube, however, shows an amplified effect at volt-

ages less than the ionization potential of the gas as was also the case with potassium tubes.

Tubes in which the photoelectric material is caesium were also made. The caesium, however, was in the form of a thin transparent film deposited on conducting metal coatings such as magnesium. The characteristics of this type of tube are shown in Fig. 7.

Tubes in which the photoelectric material is sodium have likewise been made. By following the same procedure with sodium as with potassium, tubes were made having much greater sensitivity than the potassium sulphur tubes to light of color temperature 2848° K. Moreover, the most pronounced increase in sensitivity was found to exist in the red end of the spectrum.

Fig. 8 shows a typical curve giving photoelectric current per unit of exciting light energy for such a cell. The appearance of the maximum at wave length 3600 Å may be due to some absorption of the incident light by the glass walls of the tube. The peak, however, has not been shifted appreciably by the treatment of the sodium layer with sulphur vapor. The appearance of a new maximum at approximately 5000 Å is significant.

In Fig. 9 are shown three curves comparing the sodium tube with two types of potassium cells under identical conditions showing their relative sensitivities throughout the spectral region investigated.

The maximum at low voltages appeared in the voltage vs. current curves for the sodium tubes also but at slightly higher voltages than for potassium. To make certain that this was not surface charging a point flame was applied momentarily near the edge of the tube window to spread a thin conducting film of sodium over any thoroughly non-conducting surfaces. The response of the tube to light under this condition was about double that of the surface without the film of sodium and once more the increase was chiefly in the red and infra red regions as shown in Fig. 10. The new spectral emissivity curve can be broken up into the regular curve for sodium greatly amplified plus a greatly enhanced maximum at wave length 5000 Å. In Fig. 11 is shown a history of the spectral distribution of emissions for each step in the sensitizing process.

At this stage in the development of red sensitive sodium tubes an accident was capitalized to produce a surface having the greatest response to light of any previously studied. This was due in part to another and forms the subject matter of an application of G. R. Stilwell, Serial No. 356,095, filed April 18, 1929. This new photoelectric tube was especially sensitive to long wave light, the greatly enhanced selective maximum in the spectral distribution curve broadening appreciably and the long wave limit shifting out to at least 1 μ , as shown in Fig. 12. The accident referred to was the cracking of a tube leading to an almost completely made tube, letting in air at atmospheric pressure. In repairing the crack the tube was re-evacuated. No photoelectric emission whatsoever was obtainable from the surface in that condition, but when a thin film of sodium was deposited on this surface the result was an exceptionally sensitive tube. Moreover, to prove that the resulting tube was not a freak many other tubes into which air was deliberately admitted, have been made and show the same improvement.

It appeared that the effect of air on the sur-

face was to cause a broadening of the new selective maximum on the long wave side or possibly a shift of this maximum toward the red. Fig. 13 shows that pure Na surfaces can be sensitized to long wave-lengths by air and oxygen alone, but comparison with Figs. 12 and 14 indicates the advantage of the presence of sulphur vapor. In comparing these curves, the wave shapes are alone to be considered, since the absolute values of the ordinates are not comparable.

In Fig. 15 is given the relative electron yield for a typical potassium hydride tube, a potassium cell treated with sulphur vapor, a sodium tube similarly treated, another such sodium tube with a thin film of sodium deposited on top of the dielectric and finally a sodium tube treated with both sulphur vapor and air as described above. The emissions are in terms of microamperes per lumen, and the color temperature of the exciting light is 2848° K.

The stability of the tubes was apparent when a constant light was left incident on the cathode surface for over an hour without so much as one-half of one per cent change in current output.

The linearity of response to light was checked for both potassium and sodium surfaces sensitized by the methods described above over an extended range. The variations in light intensity were effected by moving the lamp source along a photometer track. The measurements were made on a Compton electrometer, using the steady deflection method.

The words "sulphur vapor" have been used advisedly in the foregoing presentation, for it was early discovered that the actual sublimation of sulphur onto the surface was not essential. In fact, equally good tubes were made with only the volatile gases liberated from sulphur on heating. These gases could be held in a liquid air trap between the sulphur and the tube, and then by lowering the liquid air flask properly, the amount of gas actually entering the coated tube could be accurately determined.

A surprising observation was the very slight amount of gas actually necessary to produce the most sensitive tubes. Both the oil and mercury vapor pumps were left connected to the tube and running throughout the sensitizing process and the pressure of the gas on the surface was seldom higher than that to be found in most so-called "good vacua". An amount scarcely detectable with an ionization manometer gauge was effective in changing the emission immediately upon its entering the tube. The amount of gas actually occluded or contained in commercial flowers of sulphur is very small. Yet when a tube was sealed off the pump station with a side arm containing sulphur still attached, and a curve taken showing the spectral distribution of response to light (Fig. 16) there was appreciable sensitivity out to 1 μ . Evidently some gas had been liberated from the sulphur, but the amount was too small to be detected with a voltage-current curve or by any known methods.

The question as to the nature of the activating gas contained in sulphur was a challenging one since it was present in such small quantities. It certainly was not air or oxygen for these gases could not be condensed at liquid air temperatures. The assumption that it was water vapor, hydrogen sulphide or sulphur dioxide seemed most natural therefore, and tests were made checking the effect of these gases.

A large number of potassium coated and sodium coated tubes were made, the coating of each being treated with some gas in question. The chemical action and resultant color of the surface were about the only things that could be compared in the case of the various potassium tubes, all of them having selective maxima at approximately the same wave length, viz. λ 4300 Å, and the long wave limit not varying appreciably from one tube to another with one notable exception. The potassium coating on which water vapor was admitted was decidedly more red sensitive than the others. However, the surface color was decidedly different from that of the sulphur vapor tubes and the sensitivity to unresolved light not so marked.

The gas causing effects on potassium most nearly like those observed when using sulphur vapor was SO₂, the only one to give the bright golden color and the one producing the most sensitive surfaces to unresolved light. The sample used, together with the sample of H₂S, was certified by the manufacturer to have a high degree of chemical purity.

In Fig. 17, data depicting the spectral distribution of electron emission are given for potassium tubes sensitized with sulphur vapor, sulphur dioxide, hydrogen sulphide, water vapor, oxygen on sulphur vapor, tellurium vapor, phosphorous vapor and iodine vapor.

Sodium surfaces offered the most significant foundation for experiments in determining the composition of the activating gas, due to the marked variations in the shape of the spectral distribution curves for different dielectric films. Although SO₂ had appeared as the important constituent of sulphur vapor in experiments on potassium, such was not the case when sodium was the base metal. As shown in Fig. 18 the spectral distribution of sensitivity after treatments with this gas was quite different from the sulphur vapor curves. On the other hand water vapor produced curves very similar to them and the colors of the treated surfaces were quite identical, viz. a dull grey.

There seemed only one conclusion to draw from these tests. The activating gas given off from commercial flowers of sulphur must be a combination of water vapor and sulphur dioxide, and the dielectric films formed must be sodium and potassium bisulphites. This conclusion seemed the more plausible when it was recalled that the sulphonic radical SO₂.OH is an important radical in many organic dyes and that photographic plates have heretofore been sensitized to light well into the infra-red by the use of sodium bisulphite NaHSO₃. The curve in Fig. 19 was obtained from a photoelectric tube made exactly like the one from which the curve of Fig. 12 was taken except that NaHSO₃ was substituted for flowers of sulphur. The correlation of the sensitivity ranges of a photographic plate and the photoelectric tube here shown is nearly perfect and suggests that increased light absorption is the cause of increased electron emission.

There was no reason to suppose that sodium bisulphite was the only substance used in photography which could be applied to the field of photoelectricity. Accordingly, other sensitizing dyes were introduced onto the light sensitive surfaces of alkali metals, and marked increases in photoelectric emission noted. In every case the amount of dye required was very small, as in plate sensitizing, yet the colors and hues appearing on the cathode surfaces especially with the

deposition of thin top films of sodium and potassium, were many and varied.

Some of the tubes containing the dyes had to be immersed in liquid air flasks to prevent their breaking up and passing over into the cell with the action of the pump. Others had to be warmed before they sublimed, and in such cases it is not only possible but likely that partial chemical decomposition occurred. Nevertheless, the well known organic absorption radicals for the visible region, as the methyl group CH₃, the nitroxyl group NO₂, the amido group NH₂, the bromine group, the methoxyl group CH₃O, the carboxyl group CO.OH and the sulphonic group SO₂.OH, probably were fairly stable.

The first dyes used contained the sulphonic radical and were not known as photographic sensitizers. They were placed in a side tube beyond the liquid air trap 14, and then heated after the alkali metal coating was made. Upon heating some gas passed through the liquid air trap into the tube and was pumped out. This was probably nitrogen, hydrogen or possibly some hydrocarbon compound, for no chemical action with the sodium or potassium occurred. The gas retained in the liquid air trap was very effective in sensitizing the metallic surface of the tube when allowed to enter in small quantities. A very thin film of the alkali metal deposited on the colored surface always enhanced the emission. In Fig. 21 are found curves showing relative sensitivities in the visible and infra-red spectral regions of sodium cells treated with the isomeric compound tropacolin 009 No. 1 (HO.C₁₀H₆.N:N.C₆H₄.SO₃Na) and sodium indigo disulphonate. Both compared favorably with the sodium and sulphur vapor cells described hereinbefore. Curves for the corresponding potassium coated tubes, using these dyes are given in Fig. 20.

To determine whether the sensitizing process was limited to sulphur compounds, a tube was made with a rosaniline base [OH.C(C₆H₄NH₂)₃] and a sodium coating. Although no sulphur was contained in this compound, the surface treated showed a good response to light throughout the visible and near infra-red as shown in Fig. 22.

The remainder of the experiments using dyes have to do with the application of the sensitizing dyes used in photography. Because of its historical importance, having been first used to sensitize photographic plates to green and yellow light in 1882, eosin blue:



was tried first. Here was a compound containing no sulphur and no hydroxyl group, but possessing a liberal amount of iodine. Although a decided increase in sensitivity of the tubes was effected through use of this dye (Fig. 23) it was not so satisfactory as many others especially as regards response to the red light.

Unusual results in sensitizing photographic plates to red by using alizarine blue



have heretofore been claimed, such plates when treated with ammonia being reported as sensitive out to about 1μ. In Fig. 24 is found a typical curve for potassium coatings treated with alizarine blue, and in Figs. 25 and 26 other curves for potassium and sodium treated with alizarine blue and NH₄SO₃. The curve of Fig. 26 shows a decided response to light of all wave lengths under

1 μ , with the new maxima appearing at the same position as for the sulphur vapor tubes.

Similar results attended the use of dicyanine, the tubes made with addition of ammonium sulphite vapor being quite red sensitive. The exact chemical formula is unknown for this compound and other supposedly still better dyes carrying the latter part of the same word in their trade names, as Kryptocyanine and Neocyanine. From information available on these substances, it appears that Kryptocyanine should be better in the near infra-red than dicyanine which in turn should be better than cyanine ($C_{25}H_{35}N_2I$). All of these indications were borne out on photoelectric tubes, the dicyanine causing a greater electron emission from alkali metal surfaces than cyanine, and very small amounts of Kryptocyanine producing one of the broadest selective bands in the spectral distribution curve for sodium tubes so far observed. This is shown in Fig. 27.

Most of these sensitizing dyes had a tendency to volatilize spontaneously in a vacuum and the tubes containing them had to be immersed in liquid air during the later stages of evacuation of the cells. Then by lowering the liquid air slightly easily controllable amounts would pass onto the light sensitive surface. Whether or not the dyes suffered a chemical decomposition during this volatilization process is not known, but it is possible that the more complicated compounds break up into simpler ones.

While there seemed to be quite marked correlation between the absorption of the organic dyes and the photoelectric emission from alkali metal surfaces on which they were deposited, there was no evident reason for the enhanced sensitivity always appearing as a new selective maximum at the same wave lengths. Certainly the position of the new maximum seemed to be characteristic of the base metal and not the dielectric on its surface; perhaps any dielectric regardless of its absorptive properties would be sufficient to give the increased sensitivity to red light. To test this various colorless dielectrics and dielectrics practically transparent to visible light were substituted for the dyes. Most of these were liquids but could easily be held in side tubes with liquid air. The technique involved in their use was exactly identical to that for the dyes.

Acetone ($CH_3CO.CH_3$), acetic acid ($C_2H_4O_2$) carbon bisulphide (CS_2), methyl alcohol (CH_3OH) carbon tetrachloride (CCl_4), benzene (C_6H_6), chloroform ($CHCl_3$) phenyl mustard oil ($C_6H_5-N-C=S$) nitrobenzene ($C_6H_5.NO_2$) and water-vapor (H_2O) were used. Benzene and water vapor were effective in making the best photoelectric tubes, the red sensitivity of sodium surfaces properly treated with them being especially marked, as shown in Fig. 28. There was absolutely no evidence of chemical action when benzene was admitted to the tube, even though a thin film of sodium was deposited on top of it. In fact, the surface of the completed photoelectric tube looked exactly like that of pure metallic sodium. This, of course, is not surprising since the alkali metals are preserved in benzene. In contrast to the behavior of benzene on sodium was that of water-vapor, whose powerful affinity for the alkali metals necessitates their preservation in benzene, oil or sealed, air-tight containers. Yet both benzene and water-vapor have similar properties as regards increasing

photoelectron emissions from sodium and potassium surfaces.

In every case mentioned in the preceding paragraph, with the exception of that in which carbon tetrachloride was the dielectric used, there was an appreciable amount of red sensitivity developed. Moreover, the spectral distribution curves show evidence of a new peak in the photoelectric emission curve near $\lambda 5000 \text{ \AA}$ for sodium and a much less pronounced peak at $\lambda 6000 \text{ \AA}$ for potassium, these accounting for the increase in response to red light. In the case in which carbon tetrachloride was used no deflection of the galvanometer was observed when the exciting light was passed through a red filter, cutting out all wave lengths under $6000 \text{ \AA}$.

When working with carbon bisulphide (CS_2) and nitrobenzene ($C_6H_5.NO_2$) the previously described peak in the voltage-current curve at low voltages was observed in very much greater prominence. At one time during the treatment of sodium with CS_2 the current output with -15 volts polarizing voltage was four to five times its value when the polarizing voltage was increased to 100 volts.

Although the invention in the specific aspects heretofore described is independent of any theory which may be advanced to account for the results obtained, the accumulated evidence points so strongly to the theory about to be stated that it is believed to be correct, at least in its main aspects. This theory may be briefly stated as follows: Shifts in the sensitivity curves of cells employing the various materials with which the photoelectric surfaces are treated are produced by the formation of coatings which have absorption lines or bands at certain wave lengths such that when light of certain other wave lengths are incident thereon, modulation of the latter by the coating is effected to produce energy manifestations of one or more frequencies which are a side frequency or frequencies of the modulation. This side frequency, or frequencies, (which may be a sum or a difference frequency, or both, with respect to the incident frequency and the resonant modulating frequency) acts more effectively upon the photoelectric material than the incident frequency per se. This effect appears to be enhanced by employing a coating of this kind which is dipolar in nature. This may be due to the fact that the dipoles align themselves in definite geometric configurations such that there is less continual impedance to the vibrations of the molecules in the higher energy states.

The following is a discussion of the available evidence which points to this theory. The curves shown in the accompanying drawings may or may not be truly representative of the properties of that particular type of tube at its best, but they represent the properties of the tube when made according to the best technique known at the time the data was obtained. The conclusions reached provide an answer to the two main questions raised by the investigation, namely, what was the cause of the increased emission of the alkali metal surfaces bearing a dielectric film? And what is the explanation of the appearance of the new maximum peaks in the yellow (for Na) and red (for K) regions of the spectrum. Many minor questions will be treated as the discussion proceeds.

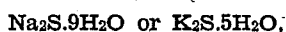
In the first place a survey of the materials used was made to determine whether or not there

existed some common constituent or element in the substances used, some activating agent common to all the dielectrics introduced on the alkali metal surfaces. Certainly, the possibility of there being traces of water vapor had to be acknowledged. Every effort was made in many cases to eliminate this condition and there was not enough present in the evacuated tubes at the time the metal coatings were made to be noticeable. But, as pointed out previously, the substances which were evaporated or sublimed onto these coatings may not have been water free. In fact, admission of admittedly moist air onto the surfaces of the sodium coatings with proper subsequent treatment greatly enhanced the emission. Moreover, the bulky, complex organic dye compounds usually were found in very fine crystalline granules, no doubt, containing water of crystallization in no small quantities, and sometimes decomposing with the actual formation of water vapor. Also, although the samples of transparent liquid dielectrics were obtained from a reliable chemical house as certified chemically pure material, there is no assurance that they were totally water free. Finally, glass blowing and vacuum pump technique are of such a nature that when a liquid frozen in liquid air is sealed onto an evacuating system at atmospheric pressure, it is impossible to entirely eliminate all traces of water from the system.

Although the amount of water vapor which could always have been present with the dielectric was admittedly small, it may not have been negligible, on the other hand, many of the experiments showed its presence to be an asset. Perhaps its presence in minute quantities was necessary, but it is quite certain that it alone was not responsible for all the increased photoelectric effects observed. So, the possibility of some moisture being present will be conceded and later it will be shown that this fits in with the explanation suggested.

The great majority of the dielectrics successfully used in these experiments were dipolar substances, or at least broke up into groups or radicals which were permanent electrical dipoles. Dipolar substances are substances, the two ends of whose molecules carry permanent electrical charges of opposite signs. Oxygen was an exception but it probably did not exist by itself on the surface, forming Na_2O or K_2O immediately. In fact, in every experiment performed except the one with benzene there appeared to be some chemical action at the surface. Now dipoles naturally are favorable to association, as pointed out by Gerlach and others, and this regular association is nothing more nor less than a preliminary stage of microcrystalline character. It is even conjectured that the very symmetrical, ring-compound, benzene, may manifest such a character upon solidifying in thin films.

Now as this microcrystalline surface structure built up, water vapor present may have been taken up as water of crystallization. Such a condition was even intimated in the case of sulphur vapor, for the hydrated mono-sulphides of sodium and potassium, as



sodium trisulphide $\text{Na}_2\text{S}_3 \cdot 3\text{H}_2\text{O}$ and the corresponding bisulphide $\text{Na}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$, are golden yellow in color, as were the surfaces of the treated

photoelectric tubes. Moreover, this water of crystallization plays a definite role in the crystal structure contributing to the vibration spectra and deporting itself generally as an actual constituent.

By the very nature of the existence of dipoles as pairs of electrical charges, it is likely that they oriented themselves on the surface in a uniform manner, such as Langmuir found for drops of oil on liquid surfaces. Moreover, the orientation would undoubtedly be one such that the eddy fields they set up at the surface would tend to oppose that due to the polarizing voltage applied. Being nearly volatile they could easily be oriented by applying a potential across the electrodes. The result would be the presence of positive charges on the alkali metal surface and negative charges slightly off the surface.

Obviously, the effect of such a surface configuration would be twofold: (1) the strong fields at the surface due to the presence of an electro-positive charge would greatly assist in pulling electrons from the metal surface, and (2) the eddy fields of the dipoles undoubtedly would direct the electrons normally outward, where the field of the applied voltage would readily accentuate this normality in tubes geometrically designed as shown. There being no anode directly in the path of the light and no polarity at the window, the photoelectrons would continue until stopped by the glass of the window on which undoubtedly would accumulate a negative charge. On the other hand, when the light was incident on the side of the tube at steep incidence, the anode was directly above the illuminated area and practically all electrons would be attracted to it.

The fact that the irregular hump in the voltage-current curves is more accentuated and at lower voltages for excitation with red light suggests that low velocity electrons were attracted to the anode more readily. It was only when the electrons were accelerated by greatly increasing the polarizing voltage that these begin to shoot past the nickel ring. In the light of this, it appears that the rather broad maxima in the curves for sodium, and their appearance at higher voltages than for potassium and rubidium, was due to the more uniform distribution of the velocities and especially the preponderance of electrons liberated by quanta of red light, as shown by spectral distribution curves. The same explanation holds for the difference in the shapes of the curves for potassium and rubidium.

If the dielectric film were allowed to build up until the metal was entirely coated, the continuous array of negative charges very likely impeded the emission of electrons. However, if at this stage a thin film of light-sensitive metal was deposited on the surface, the negative charges might well have acted as tiny grids tending to push the electrons from the illuminated film, the direction of the force being normal to the surface, also. Thus, it is seen how the layer of dipoles could function to simultaneously pull electrons from photo-sensitive surfaces beneath it and push electrons from similar films above it.

A surface structure constructed as described has striking light absorption properties, being highly selective to different bands of the visible spectrum depending on thicknesses of the various films deposited. By films or layers is not meant sharply differentiated strata. In all probability, the top film of alkali metal was formed as atoms filtered down into intermolecular space, existing

in the dielectric so that the film may have been electrically connected to the base by a multitude of conducting atomic chains. In this respect the molecular dipoles may be considered as carefully
5 planted absorption units in the light sensitive cathode surface.

That increased absorption of light was in great measure the cause of increased electron emission seemed the more likely since the presence of
10 oxygen and sulphur seemed always to improve the response to light of longer wavelengths and hydrogen alone had little effect in this region. The vibration energy of a molecule of the latter element is sufficiently great to correspond to ultra-
15 violet frequencies, whereas oxygen and sulphur in particular have vibration frequencies corresponding to colored light. The substitution of these "color molecules" for hydrogen atoms in
20 organic compounds must therefore produce increased absorption as shown by the results of these investigations. Moreover, although the vibration of an ordinary benzol molecule does not manifest itself in the visible region of the spectrum, if one or more of the hydrogen atoms is
25 replaced by color groups as NO_2 , OH , NH_2 , SO_3H etc., marked selective absorption in the visible region results. Thus the organic dyes absorb well bands of visible light because the simple ring compound benzene is a unique and distinguished
30 chemical individual with specific capacity for absorption.

A study of the selective absorption bands of the dielectrics successfully used in making photo-
35 electric tubes as herein reported, however, showed no convincing correlation with photoelectron emission. For instance, take the cases of cyanine and water vapor. Even though cyanine has a strong absorption band between λ 4500 and 6500 $\text{\AA}$ and water vapor is transparent at these wave-
40 lengths, the photoelectric emission for sodium tubes treated with water vapor was greater over this wavelength region than for sodium tubes treated with cyanine. Similar anomalies were
45 found for many other substances, benzene being a striking example. The tubes sensitized by means of this optically transparent compound manifest their best response to light at approximately the same place as cells sensitized by water
50 vapor although there is absolutely no evidence of chemical affinity between benzene and sodium as compared with the intense affinity of the alkali metals for water.

The presence of the new selective maxima in the yellow-green region of the spectrum for sodium tubes and in the orange for the potassium tubes showed that the photoelectric selectivity was unquestionably a characteristic of the alkali metal used and not the sensitizing dielectric.
60 Although the appearance of these new characteristic photoelectric maxima could not be correlated with visible absorption bands, the facts certainly pointed strongly toward an optical explanation. Investigation of the infra-red spectra of the materials used in sensitizing the tubes showed a
65 surprisingly close correlation between absorption bands there and electron emission under the action of yellow and red light. Water vapor, the sulphur compounds, benzene and organic dyes generally showed pronounced similarity in their
70 near infra-red spectra. These spectra, the vibration-rotation spectra, resolve into lines and more or less sharp bands, and are due to the vibration of positive and negative charge within
75

the molecule. It is only natural therefore that such vibration spectra should be quite characteristic of dipoles.

The materials used exhibit characteristic spectra between wavelengths 7000 and 20000 $\text{\AA}$.

Now from the data plotted as wavelength vs. current it was at once apparent that the new photoelectric maximum which appeared in the spectral distribution curve for sodium was separated from the normal selective maximum by a frequency difference corresponding to a wavelength of approximately 1μ . In other words, if the frequency of light corresponding to the new maximum were added to the characteristic vibration frequency of the molecules on the cathode surface, the summation frequency would be that corresponding to the selective frequency of pure sodium.

It appeared then that the incident light was modulated as it was absorbed by the dielectrics on the cathode surface, quanta having too little energy to liberate electrons actually acquiring more from the molecules of dielectric. As long, therefore, as the sum of the incident light frequency and the vibration-rotation frequency of the cathode materials gives a new frequency well within the limits required for the emission of electrons from the pure metal currents would be obtained. Comparison of the spectral distribution curves for pure sodium and for the sodium tubes sensitized with dielectric films (Fig. 11) on the surface showed that not only is the new peak or humps in the yellow region for the latter case separated from the original selective maximum by a wave length corresponding to a frequency of approximately 1μ , but the difference in the long wave limits for the two cases corresponded to a similar separation. Moreover, these same relations held in a certain measure for all red sensitive cells regardless of the dielectric used in the sensitizing process. Likewise the same observations carried over to the potassium cells although the magnitude of the response to red light was less.

Now if the light was actually modulated so that this summation frequency or upper side band appeared, the difference frequency or lower side band would be certain likewise to appear. In fact, it seemed more logical to conceive of the quantum yielding part of its energy to the absorbing molecule than acquiring additional energy from it. Theoretical curves were plotted for the ultra-violet, visible and near infra red and show that the original curves of one selective maximum are changed to curves having three maxima and that the humps in the visible agree with the experimental curves of the accompanying drawings.

Since in the visible region the effective change is produced by the incident light acquiring energy from the absorbing molecule, it is likely that many of them exist in the higher energy state. It appears, therefore, that the vibration-rotation frequencies characteristic of di-poles may be far less damped when existing, as it is surmised they do, in the micro-crystalline films on the surface.

Throughout this application the convention has been followed, in symbolically indicating the nature of the cathodes, of using the chemical symbols for designating the materials used, the symbol for the base layer of photoelectric material appearing first.

The following materials have been used in making tubes according to this invention:

KSH
 KHS
 5 KNSH
 KTe
 KTI
 KSe
 NaSe
 10 NaI
 KBIH
 NaCl
 NaP
 KAs
 15 KH₂SO₄
 KO
 NaCO₂
 NaSN
 KSO₂(H₂O)
 20 TiNaS
 KSN
 KP
 NaSe (Air)
 KSO
 25 K(NaSO₃)
 K (Indigo Disulphonate)
 NIKS Air
 Na Eosin
 NaNH₃SO₃
 30 NaS plus NH₃SO₃
 KNH₃SO₃
 KS plus NH₃SO₃
 Na dicyanine
 Na dicyanine plus NH₃SO₃
 35 K dicyanine
 K dicyanine plus NH₃SO₃
 KH on copper oxide
 Rb (Alizarine blue) plus NH₃SO₃
 K (Kryptocyanine)
 40 Ag Kryptocyanine Na (Kryptocyanine)
 Na cyanine
 K cyanine
 K nitrobenzene plus sulphur
 Na nitrobenzene plus air
 45 Na plus CS₂ on Pt
 Na plus spirits of turpentine
 Na plus acid benzene sulphonic
 Na plus neocyanine
 Na plus neocyanine plus H₂O.

50 It may be that the modulation referred to in this specification is one wherein the energy of the side frequencies manifests itself only in the form of the emitted electrons and does not appear as light of new wave length. The term "side frequency" as herein used is therefore not intended to be limited in this respect to the case where light of new wave lengths is produced.

55 The term "light" as herein used is intended to cover not only light within the range of the so-called visible spectrum but also electromagnetic radiations both above and below that range.

60 The term "equi-energy" curve is meant to mean a curve wherein the ordinate refers to photoelectric emission per unit of incident light of a particular wave length. In the accompanying drawings the curves plotted between wave length and photoelectric current per unit of impressed energy are equi-energy curves.

65 The term "alkali metals" as herein used is intended to cover the alkaline earth metals.

What is claimed is:

70 1. A photoelectric tube having an anode and a cathode comprising a photoelectric substance sensitive to visible light and a light receiving layer of dielectric material in contact therewith

formed by exposing said substance to the action of sulphur vapor.

2. A photoelectric tube having an anode and a cathode comprising a photoelectric substance sensitive to visible light and a light receiving layer of dielectric material in contact therewith formed by exposing said substance to the action of sulphur vapor and water vapor.

3. A photoelectric tube having an anode and a cathode comprising a layer of light sensitive material in contact with a layer of dielectric produced by vaporizing an organic dye and bringing the vapor into contact with said light sensitive layer.

4. The process of making a cathode for a photoelectric tube having an anode and a cathode which comprises producing said cathode by forming in vacuo a layer of photoelectric material sensitive to visible light and exposing the surface of said layer to a gas which produces thereupon a layer of dielectric other than a hydride of said photoelectric material.

5. The process of making a cathode for a photoelectric tube having an anode and a cathode comprising producing said cathode by forming in vacuo a layer of photoelectric material sensitive to visible light and exposing the surface of said layer to sulphur vapor.

6. A photoelectric tube having an anode and a cathode comprising a layer of alkali metal in contact with a layer of dielectric produced by vaporizing an organic dye and bringing the vapor into contact with said layer of alkali metal.

7. A photoelectric tube having an anode and a cathode comprising a relatively thin layer of solid alkali metal in contact with a layer of dielectric produced by exposing the surface of said layer of alkali metal to the vapor of a colorless dielectric which is liquid at ordinary room temperatures.

8. A photoelectric tube having an anode and a cathode comprising a layer of alkali metal in contact with a layer of dielectric produced by exposing the surface of said layer of alkali metal to the vapor of alizarine blue.

9. The process of making a cathode for a photoelectric tube having an anode and a cathode comprising producing said cathode by forming a layer of alkali metal in vacuo, and exposing the surface of said layer to the vapor of an organic dye.

10. The process of making a cathode for a photoelectric tube having an anode and a cathode comprising producing said cathode by forming a layer of alkali metal in vacuo, and exposing the surface of said layer to the vapor of alizarine blue.

11. A photoelectric tube having an anode and a cathode comprising a photoelectric substance of the alkali metal group and a light receiving layer of dielectric material in contact therewith formed by exposing said substance to the action of sulphur vapor.

12. A photoelectric tube having an anode and a cathode comprising a photoelectric substance of the alkali metal group and a light receiving layer of dielectric material in contact therewith formed by exposing said substance to the action of sulphur vapor and water vapor.

13. A photoelectric tube having an anode, and a cathode comprising a relatively thin layer of caesium and a deposit of dielectric material thereon formed solely by exposing said layer of caesium to the action of gas given off from a dielectric material.

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