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Kaspaul

[11] **3,721,496**

[45] **March 20, 1973**

[54] **IMAGE EXPOSURE AND DEVELOPMENT METHOD**

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[73] Assignee: **Hughes Aircraft Company**, Culver City, Calif.

[22] Filed: **Feb. 4, 1972**

[21] Appl. No.: **223,533**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 115,943, Feb. 17, 1971, Pat. No. 3,664,249.

[52] **U.S. Cl.** ....**355/77,** 96/48 R, 117/17.5

[51] **Int. Cl.** **G03b 27/32**

[58] **Field of Search**...355/27, 77, 106, 132; 95/89 R, 95/89 G, 94 G; 96/48 R; 117/17.5; 118/49

[56] **References Cited**

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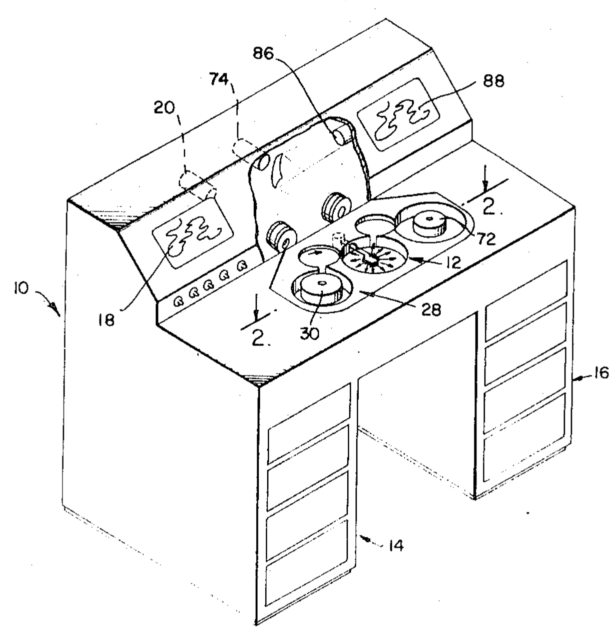
Primary Examiner—Samuel S. Matthews
Assistant Examiner—Fred L. Braun
Attorney—W. H. MacAllister et al.

[57] **ABSTRACT**

The image exposure and development method of this invention comprises: the steps of exposure of a sensitive medium which is developable by the deposition of atoms thereon, feeding the exposed medium to wrap around a major portion of the circumference of spaced discs, and directing a vapor flux between the discs to impinge upon the medium so that the latent image thereon is developed by selective acquisition of the metal onto the surface.

6 Claims, 11 Drawing Figures



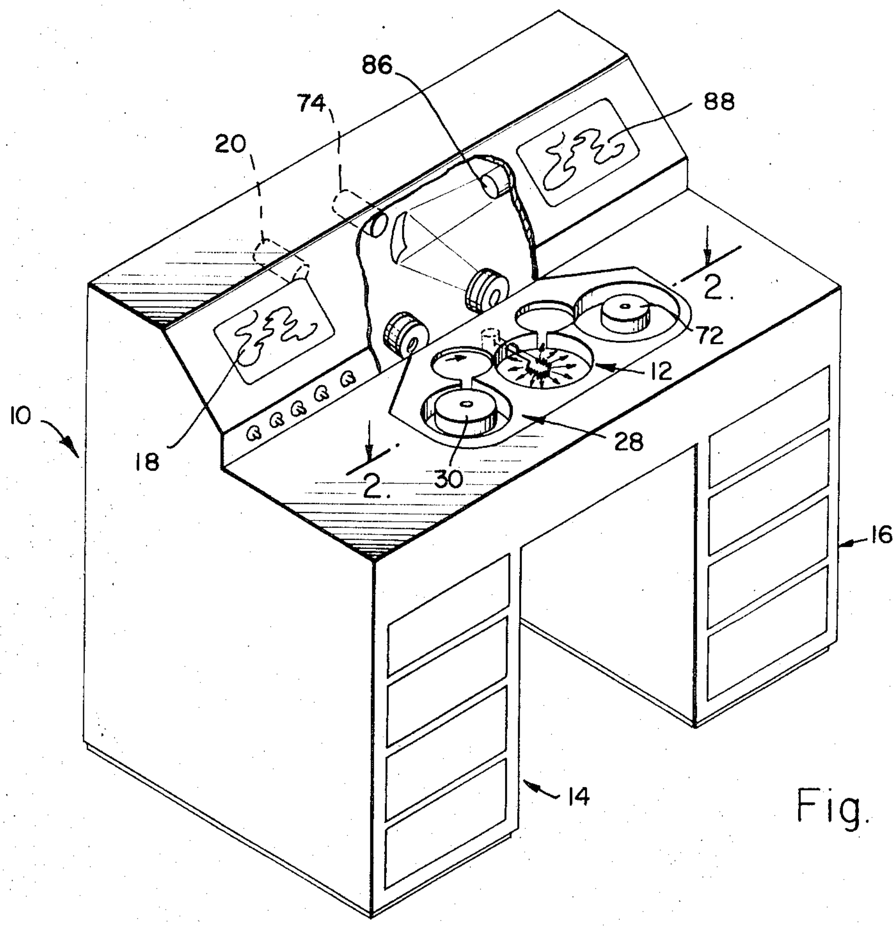


Fig. 1.

Fig. 3

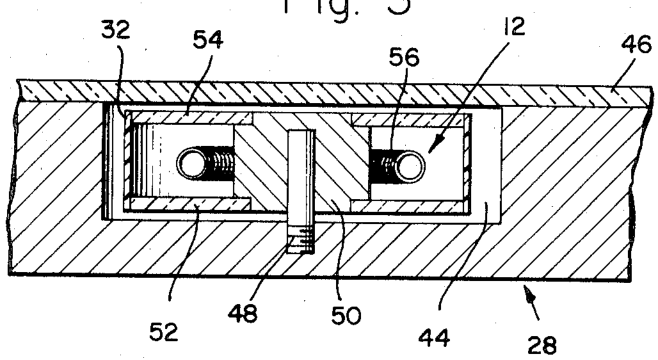
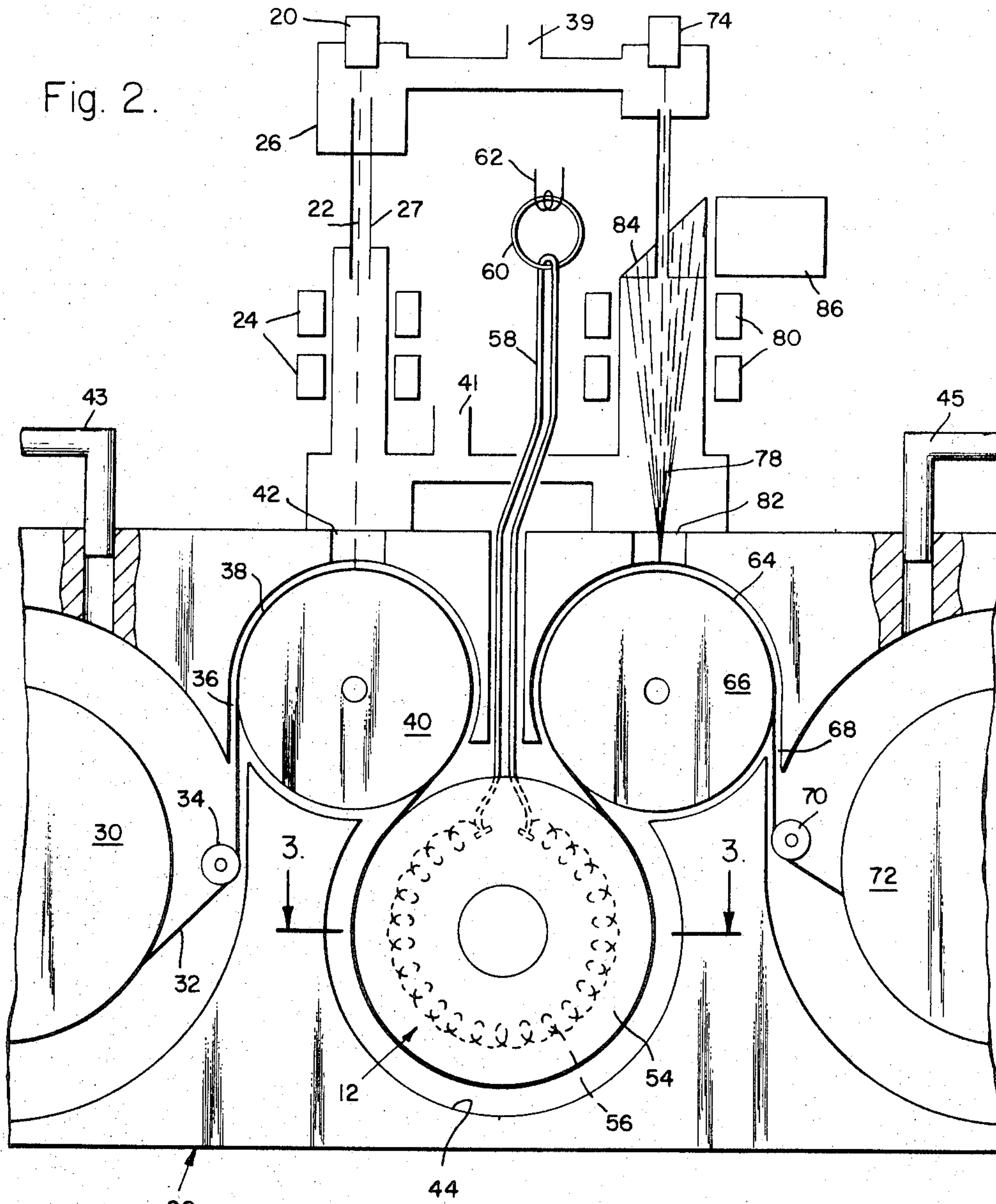


Fig. 2.


20
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44
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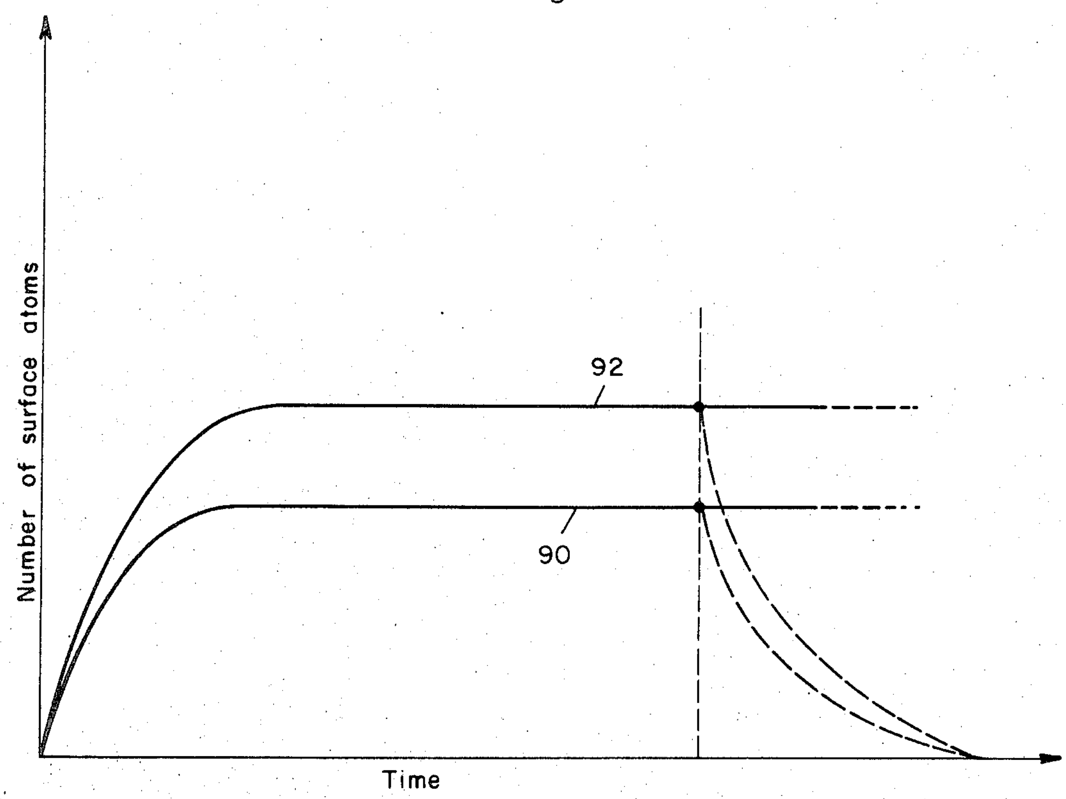
Fig. 4a.



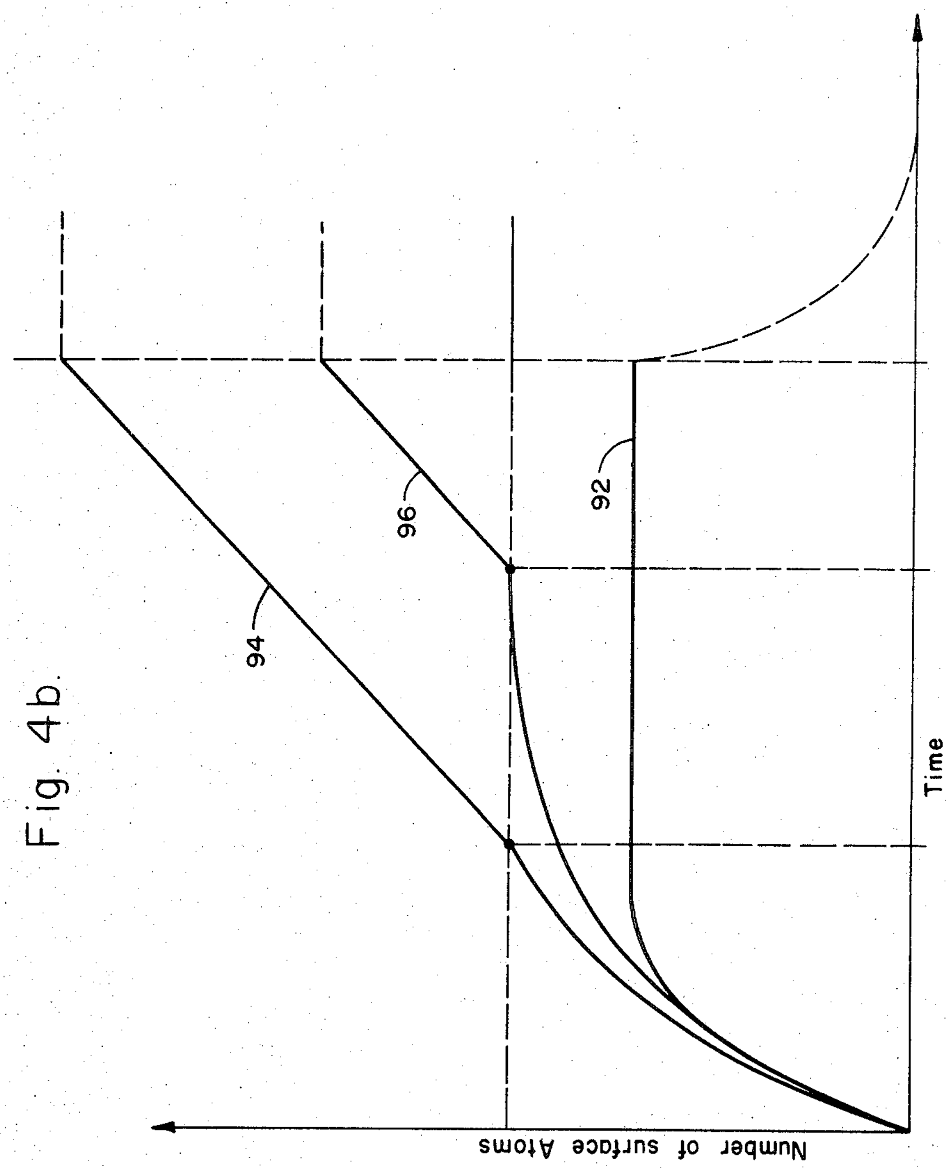


Fig. 4b.

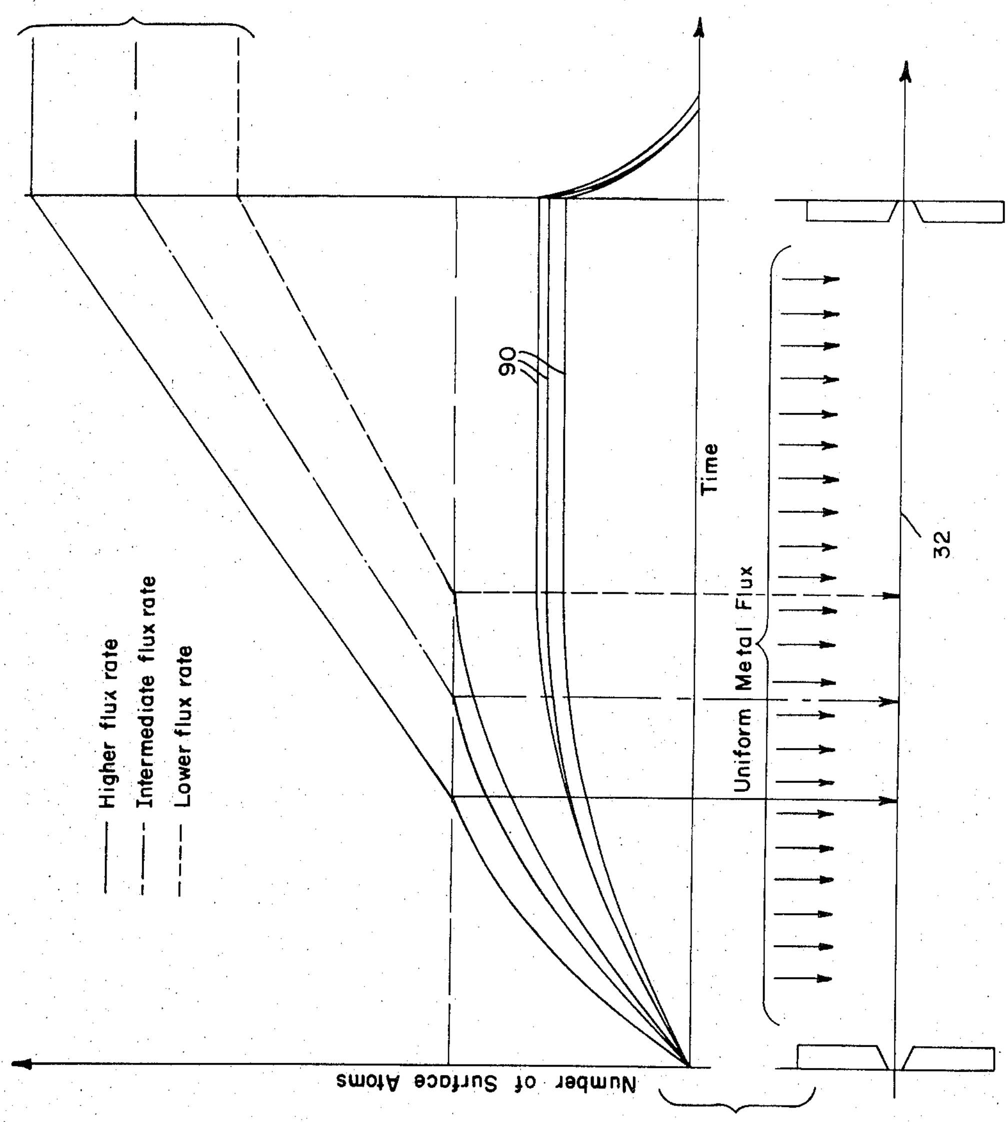

Higher flux rate
Intermediate flux rate
Lower flux rate
90
Time
32
Uniform Metal Flux
Number of Surface Atoms

Fig. 4c.

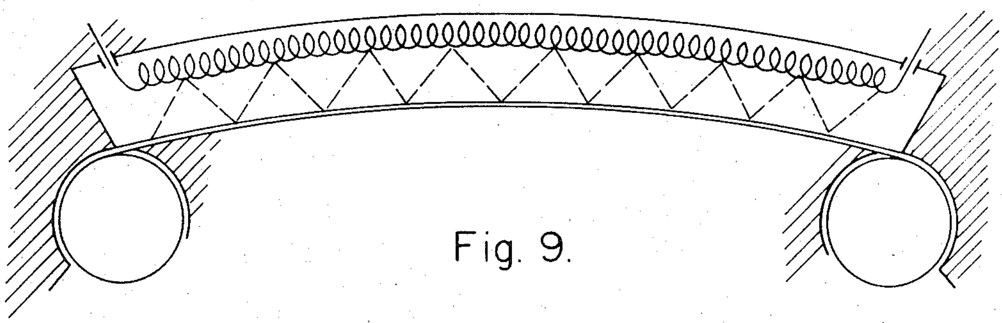
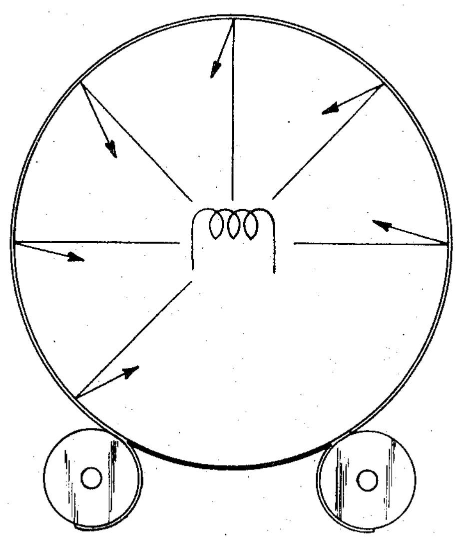


Fig. 9.

Fig. 5.



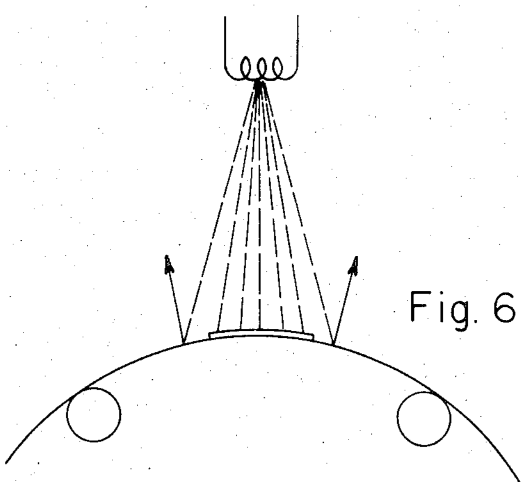


Fig. 6. PRIOR ART

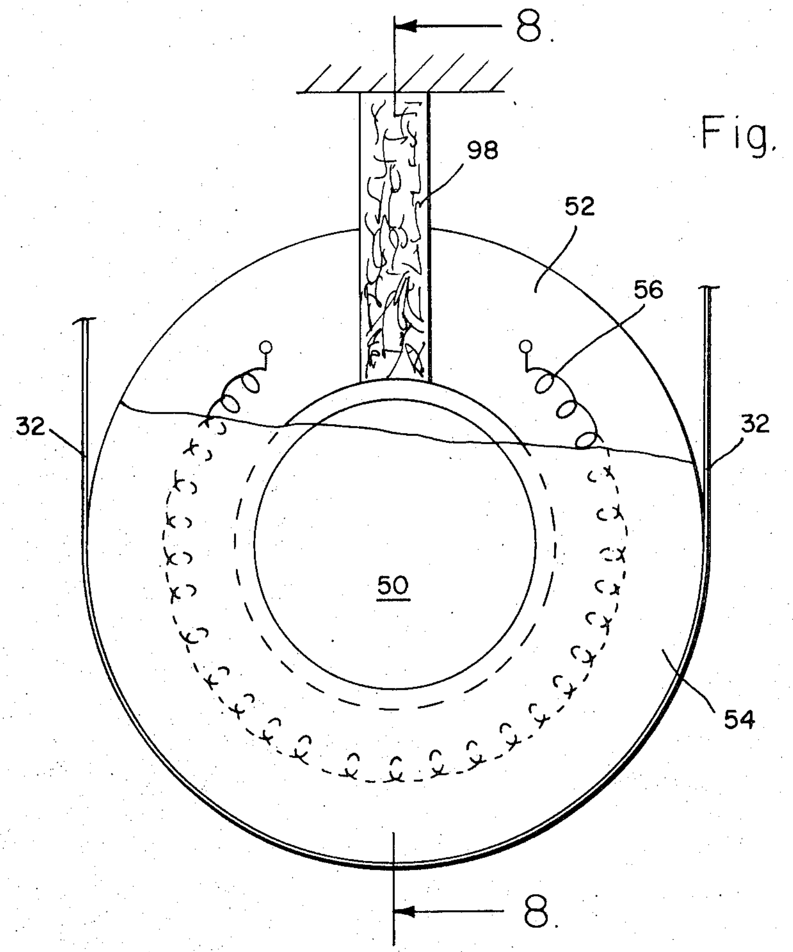


Fig. 7.

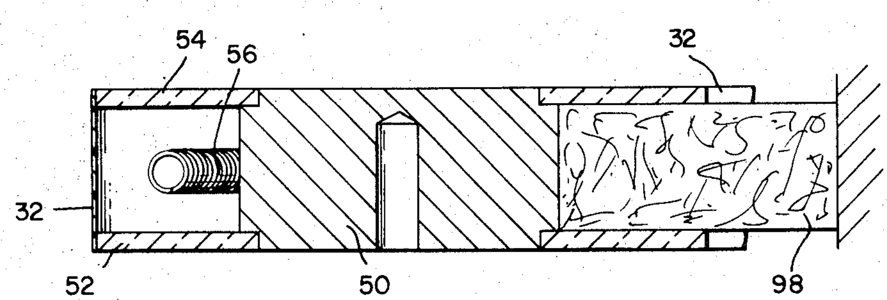


Fig. 8.

IMAGE EXPOSURE AND DEVELOPMENT METHOD

CROSS REFERENCE

This application is a continuation-in-part of patent application Ser. No. 115,943, filed Feb. 17, 1971, now U.S. Pat. No. 3,664,249, which, in turn, was a division of the application which resulted in U.S. Pat. No. 3,585,965.

BACKGROUND

This invention is directed to a method for exposing and developing a photosensitive medium to produce a latent image thereon and to develop the latent image into a visible image by means of the selective deposition of metal atoms thereon from a vapor.

A number of prior art processes for the recording of information and subsequent formation of visible images employ the selective deposition of various materials into latent images. An example of this is found in A. F. Kaspaul et al. U.S. Pat. No. 3,235,398, granted Feb. 15, 1966. A number of other inventions are directed to the same general type of process. These processes employ the selective deposition of metal atoms to create the visible image. A. F. Kaspaul et al. U.S. Pat. No. 3,140,143, granted July 7, 1964, describes the use of a metal chosen from Group II–B of the periodic system as a metal which can be employed with the particular substrate disclosed therein. Selective deposition can be accomplished on suitable substrates by the employment of a variety of other materials as they are discharged from a boiler or any other suitable source. Additionally, a metal chosen from Group I–B or magnesium is suitable and can be employed in the same way. In other cases, the developer material is provided by the dissociation of a metal-containing compound, such as silane. Furthermore, cadmium sulfide, lead sulfide, bismuth trioxide may be deposited in imagewise fashion to produce active elements for microcircuitry applications, as described in A. F. and E. E. Kaspaul U.S. Pat. No. 3,333,984, granted Aug. 1, 1967. Additionally, while the three cited prior patents describe the selective deposition of metals, metal chalcogenides, etc., for image production, such deposition can be employed for other purposes, such as providing a conductive path, or the like.

The prior art teachings are directed to batch-type processing, as well as toward continuous applications. However, they have not resulted in efficient employment of the vaporized materials at high processing speeds. Accordingly, in the prior art applications, a sizeable fraction of the "developer" is deposited within the development chamber rather than onto the substrate. Thus, in continuous usage, material is wasted and frequent cleaning is necessary.

SUMMARY

In order to aid in the understanding of this invention, it can be stated in essentially summary form that it is directed to an image exposure and development method which includes the steps of exposure of a nucleation-sensitive material to create a latent image thereon, followed by continuously feeding the medium to a development chamber which is defined by first and second circular closure plates which define the ends of

the development chamber and wrapping the medium substantially around the closure plates to form the radial confines of the chamber, and development of the latent image by directing a metal vapor source onto the exposed medium to make the latent exposure visible.

Accordingly, it is an object of this invention to provide an image exposure and development method which is arranged for the exposure of and subsequent development of various medium by the deposition thereon of selected materials to form a visible image faithfully reproducing the information exposed on the medium to form latent, invisible images on the medium. It is a further object of this invention to provide an image exposure and development method wherein a portion of the chamber wall is formed by other than the medium and is at such conditions, and the developing vapor flux is adjusted to such a rate that stable deposition does not take place on any of the walls of the chamber except the wall formed by the medium. It is still another object of this invention to provide an image exposure and development method which employs first and second spaced discs and the medium embraces a large portion of the circumference of the discs to define the image exposure and development method and apparatus therein. It is a further object to provide an exposure and development method wherein continuous development is accomplished at nearly **100** percent efficiency. Other objects and advantages of this invention will become apparent from a study of the following portion of the specification, the claims, and the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is an isometric view of a recording and playback console employing the preferred embodiment of a structure for employing the image exposure and development method of this invention.

FIG. **2** is an enlarged partial section taken generally along the line **2—2** of FIG. **1**.

FIG. **3** is a partial section taken generally along the line **3—3** of FIG. **2**.

FIGS. **4***a*, **4***b*, and **4***c* are graphs showing various conditions under which selective deposition of atoms and molecules will occur.

FIG. **5** is a schematic view of the development chamber of this invention showing development vapor paths.

FIG. **6** is a schematic view of a prior art development chamber showing development vapor paths.

FIG. **7** is a schematic view of the development chamber of this invention showing an optical wiper therein.

FIG. **8** is a section on the line **8—8** of FIG. **7**.

FIG. **9** is a schematic view of another embodiment of the development chamber of this invention.

DESCRIPTION

A recording and playback console **10** incorporates the development chamber **12** of this invention Console **10** includes housing spaces **14** and **16** for electronics. It is electrically connected and arranged to receive an electronically defined image which can be visually displayed on the face of cathode ray tube **18**. In other words, the console receives images and sound in the form of electronic signals resulting from various sources commonly employed in conventional television practice. The purpose of the console is to receive, record, and to play back these signals in a desired line frequency.

An electron source **20** produces a modulated beam **22** in accordance with the input signals. Beam **22** is focused and deflected by any conventional electrostatic or electromagnetic means, such as focusing and deflection means **24**. However, rather than producing orthogonal scan, only lateral scan corresponding to the horizontal scan on the image is produced by the deflection means. Housing **26** encloses the beam and is pumped to a suitable low pressure at the pump connections indicated for satisfactory beam performance. Drift tube **27** permits beam passage.

As is seen in FIG. **2**, tape deck **28** includes a supply of recording tape on reel **30**. The tape **32** passes around exit guide roll **34** through slot **36** into a very narrow gap of chamber **38**. Capstan **40** rotates simultaneously with capstan **66** within chamber **38**, wrapping the tape **32** around its circumference. The width of slot **36** and the clearance around recording tape **32** as it moves around the capstan **40** within chamber **38** is minimized to reduce pumping requirements. Opening **42** in tape deck **28** permits beam **22** to impinge upon media **32** as it moves past opening **42** to thus create a latent image on the recording media. Since tape deck **28** and opening **42** are evacuated to different vacuum levels, the narrow spaces in chamber **38** are sufficient to maintain the desired pressures for each area.

Differential pumping of the recording/readout chambers and the respective gun areas is preferably utilized to minimize the size requirements of the vacuum equipment. FIG. **2** shows an arrangement whereby the gun areas may be held at $\leqq 10^{-6}$ Torr with a 2 inch diffusion pump by connection to port **39**, whereas the recording/readout chambers are maintained at 10^{-4} Torr with a 3 inch booster pump by connection to port **41**. Development chamber **44** and tape reel chambers of the tape deck **28** operate at $\leqq 10^{-2}$ and $\leqq 10^{-1}$ Torr, respectively, by use of forepumps connected to ports **43** and **45**.

From chamber **38**, the media **32** passes into the stationary development chamber **44** in which the rotating development chamber **12** is located. As seen in FIG. **3**, chamber **44** is closed by transparent cover **46** so that the progress of development can be observed. Bearing post **48** is centrally mounted in recess **44**, and hub **50** is rotatably mounted thereon. Circular discs **52** and **54** are mounted upon hub **50** so as to rotate therewith. Preferably, upper disc **54** is conveniently removable from the hub and is transparent for visibility purposes. Tape **32** passes around discs **52** and **54** so that the edges of the medium are engaged thereby, and the discs, together with the hub, are rotated as the medium passes through the stationary development chamber **44**. Tape **32** engages around a substantial part of the circumference of the discs, as shown in FIG. **2**, to define the rotating development chamber **12** enclosed by the medium and the discs.

Source **56** is the source of atoms and/or molecules for the development of the latent images contained within the medium **32**. Source **56** is conveniently a heated coil or mesh which is connected by leads **58** to the secondary of transformer **60**. Energization of leads

62 to the primary of transformer **60** causes high current flow through the coil which forms source **56**, thereby heating it to the proper temperature. When the coil or mesh is plated with the metal to be vaporized, such as zinc or cadmium, 10 watts is sufficient to develop a 35 mm tape at 36 inches/second, and one coil or mesh can have sufficient material to develop more than several thousand feet of tape. Of course, other vapor sources may be employed, e.g., a small boiler could be used to supply the required vapor for many tape reels. Source **56** is preferably positioned so that it is spaced equal distance from all points of the tape as the tape is wrapped around the discs to form the development chamber.

The developer source may be of any type and shape and will successfully operate as long as it is centrally located. Of course, an eccentric positioning is possible, if one adjusts the efflux pattern accordingly.

After leaving stationary development chamber **44**, the now developed tape is transported to chamber **64** where it engages around capstan **66**. After leaving capstan **66**, tape **32** passes through slot **68** and around guide roll **70** to be wound on tape reel **72**. If reading of the image is required immediately following recording and development, it may be accomplished with the readout gun **74** scanning across the tape on capstan **66**. Electron gun **74** in housing **76** directs an electron beam **78** onto the image-carrying medium. Focus and deflection means **80** scans the electron beam laterally across the tape as it moves past opening **82**. As a result of electron impingement, photons are emitted in accordance with the image content of the medium. These photons are focused by mirror **84** onto photomultiplier **86**. The image is thus returned to an electronic signal and can be rebroadcast in a different line frequency and/or cathode ray tube **88**. Housing **76** is suitably evacuated for proper electron beam conditions, and the narrow spaces around the medium in chamber **64** permit the maintenance of a proper vacuum with minimal pumping equipment.

The usefulness of this invention may best be understood by exposing a given surface to an incident flux of atoms and/or molecules from a molecular oven or other vapor source. Atoms and/or molecules will condense upon the surface, at first moving about it in random fashion. They are eventually captured by active sites to form a stable deposit, or re-evaporated from the surface after a certain time has elapsed. At low incident rates, a certain number of atoms will be found upon the surface at any given time so that the equilibrium concentration is reached as soon as the re-evaporation rate equals the incident flux. At equilibrium,

$$n_e = n_i = N_{ad} A \cdot \exp(-\phi ad/RT)$$

or

$$\log(n_i/N_{ad}) = \log A - (0.434) \cdot \phi ad/RT$$

n_i = Incident flux, [atoms · cm^{-2} · sec^{-1}]
n_e = Re-emitted atoms, [atoms · cm^{-2} · sec^{-1}]
N_{ad} = Number of surface adsorbed atoms, [atoms · cm^{-2}]
A = Frequency constant $\approx 10^{14}$ for most metals
ϕ_{ad} = Estimated heat of adsorption, [Kcal · $mole^{-1}$]
R = Gas constant [1.987 cal · deg^{-1} · $mole^{-1}$]
T = Temperature in degrees Kelvin [°K]

Using zinc for the incident atoms and a glass surface held at 300° K as the receptor,

$$\log (n_i/N_{ad}) = 12.3$$

Using this value, surface concentrations of 10^5 or 10^7 atoms/cm^2 are obtained with incident rates of 10^{17} or 10^{19} atoms/cm^2 · sec. It may be assumed that up to surface coverages of $\theta \leqq 10^{-8}$ ($\theta = N_{ad}/N_{pl}$; N_{pl} = number of possible surface sites in an orderly lattice) no stable twins or even triplets will be produced which have a much longer lifetime than single atoms, thus all atoms will eventually leave the surface, especially upon cessation of the incident flux. In FIG. 4*a*, curves **90** and **92** indicate this for the two concentrations of 10^5 and 10^7 atoms/cm^2, respectively. Hence, the two glass discs of the development chamber should be free of zinc deposits as long as the surface coverage is kept below 10^{-8}, and spurious nucleation centers are avoided. FIG. 7 shows a simple solution for the prevention of random nucleation centers in the rotating development chamber.

As previously indicated, the recording tape containing the latent images forms a substantial portion of the development chamber and is therefore exposed to the incident flux of zinc atoms, as long as it surrounds the two glass discs and the developer source. During this time interval, atoms and/or molecules will condense and re-evaporate from its surface which has, with the exception of the latent images, quite similar surface properties as those of the glass discs. Hence, no condensation occurs upon the "background" of the medium.

However, electrons previously impinged upon the medium have created latent images characterized by areas of much greater heat of adsorption for zinc. At an incident flux of about 10^{19} atoms/cm^2 sec., these invisible images develop into visible images, in less than one second, if one assumes that ϕ_{ad} is about 12 K cal/mole for an average portion of the latent image, thus

$$\log (n_i/N_{ad}) = 5.5$$

The corresponding surface concentration amounts to nearly 10^{14} atoms/cm^2 ($\theta = 10^{-1}$) which is much too large to maintain equilibrium condition, hence rapid formation of twins, triplets and stable cluster occurs and continuous film growth is only a matter of time.

Because the previous electron beam incidence upon the tape has modulated the number of nucleation sites, their effective energy and distribution, ϕ_{ad} varies with the information content and one obtains a time dependence of the onset of permanent condensation. This is illustrated in FIG. 4*b* by curves **94** and **96**, assuming a constant incident rate. Curve **94** represents a large exposure to electrons, curve **96** a smaller amount of irradiation, and curve **92** the unexposed background of the tape. The critical surface concentration of about 10^{14} atoms/cm^2 was found experimentally; at this point, the re-evaporation rate drops rapidly to zero and every incoming atom must be captured. By carefully controlling the zinc flux and the development speed, all zinc atoms are eventually deposited upon the recording tape without any loss of material to adjacent areas. Furthermore, by the very nature of the rotating development chamber, any rise of the incident rate does not precipitate the deposition of zinc on unwanted areas, because the process is self-regulating. This is best explained by FIG. 4*c*.

As shown, the tape enters the rotating development chamber on the left and is immediately exposed to a uniform zinc flux. Depending upon the image content, it will take a certain time for even the most energetic centers to take full control over the deposition process, faithfully reproducing the desired information.

For all practical purposes, the time interval from the first exposure of the tape to the zinc vapor to the onset of barely visible images ranges from about 0.25 to 0.75 of the total time spent in the development chamber.

Normally, the onset of visible condensation is chosen to be at about midpoint in the development chamber by adjusting the incident rate accordingly, hence a rise or fall of the number of incident atoms due to various demands of the tape will only shift this point either forward or to the rear without affecting anything else except the final optical density of the images, Curves **90** show the background at the several flux rates, while the upper curves show the image deposition at the several flux rates. If unexposed tapes are fed into a development chamber while maintaining a steady efflux from the developer source, the number of available zinc atoms must increase within the volume of the chamber resulting in an excessive incident rate. With the rare exception of the rotating chamber configuration, autonucleation proceeds indiscriminately in the system and suddenly zinc atoms will condense everywhere. At excessive incident rates, the rotating chamber seldom becomes coated and the tape will always pick up the zinc, even though it has not been exposed to electrons. This is made possible by the most favorable arrangement whereby the tape circles the developer source.

FIGS. **5** and **6** show two extremes, in each case utilizing a filament type zinc source. The FIG. **6** is typical for prior art arrangements and large incident rates are required to produce visible images in the shortest possible time. About 80 percent of the atoms may be lost at TV-recording rates, whereas, by using the rotating development chamber, all re-evaporating atoms are collected eventually by other portions of the tape. Of course, a modified development system may be constructed whereby a uniform zinc flux is established over a length of tape. However, this is not a simple approach and requires not only a large area source, as is shown in FIG. **9**, but also a sizeable backup surface. Since this "-zinc reflector" is not renewed, it may become coated in time and adsorbs all the zinc available. In comparison, the "dead area" in the rotating chamber of this invention is quite small, and the developer flux incident upon it is far below critical. Furthermore, the two rotating glass discs, as well as the hub, may be fitted with a stationary wiper or protection means, as shown in FIGS. **7** and **8**. This felt-type rectangular wiper block **98** may be soaked in a suitable organic liquid of low free surface energy, thus providing continuous protection for the wiped surface from zinc deposition.

In order to minimize the chance of permanent zinc deposition on the interior surfaces of the discs defining the chamber, and to prevent permanent deposition where the critical conditions have been just reached, protection means can protect a small area of the interior surfaces of the discs. This protection means provides an area in which a vapor flux is not directed at the discs and permits a zone of evaporation without corresponding impingement. The wiper **98** provides such a protected area and would be helpful in preventing zinc buildup, even if it did not contact the discs. Instead of the wiper **98**, or additionally to the wiper **98**, a disc protection means comprising a stationary thin plate located adjacent to the interior surface of each disc and adjacent to the position of the wiper can be employed. Such a plate might be a truncated circular segment, or pie-shaped piece to provide protection means for the discs, as discussed above.

The kind of recording medium is not critical. As a matter of fact, anything that has a controlled variation of the surface-free energy upon it may be developed in this manner. The preferred media for electron beam recording/readout in near real time is comprised mainly of photoconductive and photoemissive pigments combined with a nucleation-inducing compound in a suitable binder. Decomposable compounds yielding nucleation centers of desired configurations upon electron, photon, or ion bombardment may also be utilized.

This invention having been described in its preferred embodiment, and an alternative embodiment also described, it is clear that it is susceptible to numerous modifications and embodiments within the ability of those skilled in the art and without the exercise of the inventive faculty. Accordingly, the scope of this invention is defined by the scope of the following claims.

What is claimed is:

1. The method of exposing and developing a sensitive material on an indefinite length of moving web to form a latent image on the web and subsequently develop the latent image to a visible image comprising the steps of:

continuously feeding a sensitive medium on a web past an exposure station;

directing exposure energy selectively at the medium as it passes the exposure station to form a latent image on the sensitive medium so that the exposed area of the sensitive medium has a greater heat of adsorption than the unexposed area;

continuously feeding the web to and engaging the web around a pair of axially-aligned rotatable discs so that the latent image faces inward between the discs, and the continuously feeding web rotates the discs and forms the unobstructed circumference of the development chamber;

producing a flux of vaporized developer material between the discs to deposit on the web to develop the latent image and thereby form a visible image.

2. The method of exposing and developing a sensitive material of claim **1** further including the step of protecting a zone between the discs from the flux of vaporized developer material so that the inward surfaces of the discs are protected from the flux as the discs pass the zone.

3. The method of exposing and developing a sensitive material of claim **1** further including the step of controlling the surface conditions of the inwardly-directed faces of the discs so that the surface concentration of the developer material on those faces of the discs is below 10^{14} atoms/cm^2.

4. The method of exposing and developing a sensitive material in accordance with claim **3** wherein the exposure step of the medium is controlled to cause a sufficient increase in the heat of adsorption of the developer material to cause deposition of developer material on the latent image area in excess of about 10^{14} atoms/cm^2.

5. The method of exposing and developing a sensitive material of claim **4** further including the step of protecting a zone between the discs from the flux of vaporized developer material so that the inward surfaces of the discs are protected from the flux as the discs pass the zone.

6. The method of exposing and developing a sensitive material in accordance with claim **5** further including the step of removing deposited developer material from the inwardly-facing faces of the discs at said zone.

* * * * *