

[54] **PROCESS FOR NONDESTRUCTIVELY TESTING WITH RADIOACTIVE GAS USING A CHILL SET SEALANT**

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[51] **Int. Cl.** ..... **G21h 5/02**

[58] **Field of Search**..... **250/302, 303, 304**

[56] **References Cited**  
**UNITED STATES PATENTS**

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Kryptonates: A New Technique for the Detection of Wear, by Cucchiara et al., from Materials Evaluation May 1967, pgs. 109-117.

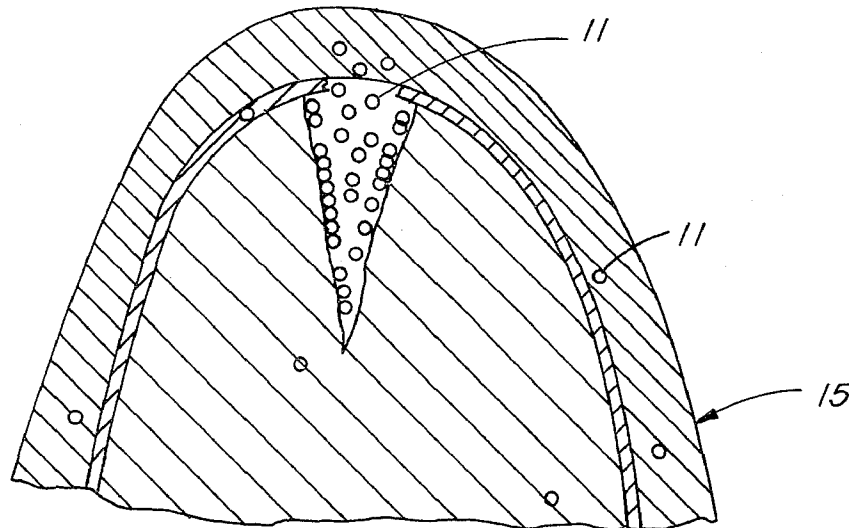
KR<sup>85</sup> becomes a Universal Tracer, by Chleck et al., from Nucleonics, July 1963, pgs. 53, 54, 55.

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[57] **ABSTRACT**

An article surface is nondestructively tested for substantially invisible surface voids by adsorbing a radioactive gas thereon. The adsorbed radioactive gas is disproportionately retained on those surfaces presented by the substantially invisible surface voids as compared to the remaining surfaces of the article contacted by the radioactive gas. The radiation released by the radioactive gas remaining adsorbed is used to identify the substantially invisible voids. To immobilize the radioactive gas adjacent or within the surface voids, a sealant composition is provided which is capable of being chill set. The temperatures of the article surface to be tested and the sealant composition are then related so that the article surface is at a temperature below the chill set temperature of the sealant composition and the sealant composition is at a temperature above its chill set temperature. The article portion to be tested is then coated with sealant composition to form a chill set coating thereon of substantially uniform thickness.

10 Claims, 3 Drawing Figures



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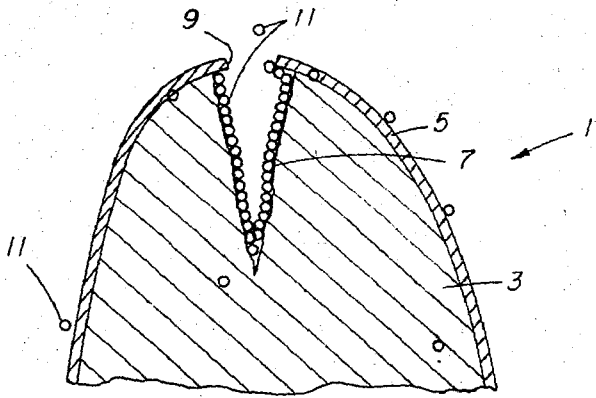


FIG. 1

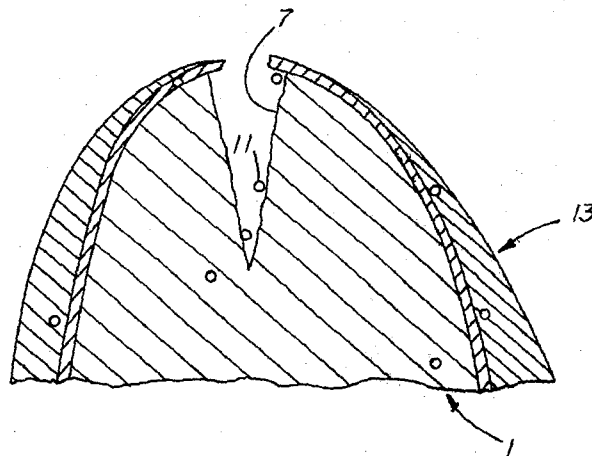


FIG. 2

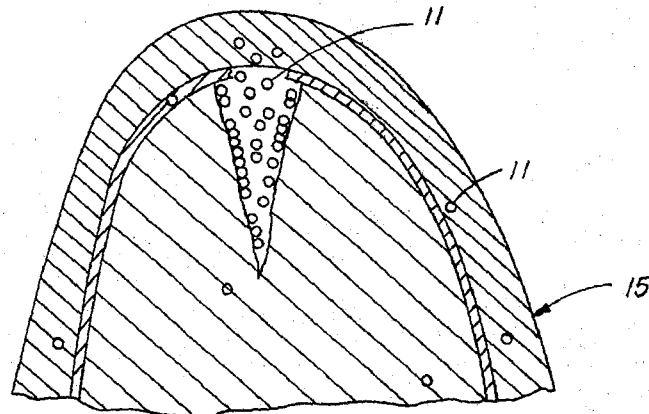


FIG. 3

## PROCESS FOR NONDESTRUCTIVELY TESTING WITH RADIOACTIVE GAS USING A CHILL SET SEALANT

This invention relates to an improvement in a photographic process in which selectively adsorbed radioactive gas is used to identify surface voids. More specifically, this invention relates to an improvement in such a process in which the retention of radioactive gas within or adjacent the surface voids is enhanced.

Eddy U.S. Pat. No. 3,621,252, issued Nov. 16, 1971, teaches a process for nondestructively testing an object for surface defects by selectively adsorbing radioactive krypton gas within any defects present. The radiation emitted by the adsorbed gas can be detected and recorded in a variety of ways to determine the presence of surface defects and, if present, their size and location. The Eddy process is disclosed to be an improvement over prior radioactive gas sorption techniques, since it relies primarily upon adsorption rather than absorption, thereby producing a sharper definition of the surface defect.

While the Eddy process is highly useful in detecting surface defects of very small size, it has the disadvantage that adsorbed gas is readily released from object surfaces. In fact, Eddy relies upon the disproportionate release of adsorbed gas from object surfaces other than those presented by surface defects in order to find the defects. The larger the surface defect which the adsorbed gas has entered, the more likely it is to be released therefrom. Thus, with the Eddy process defect detection rapidly becomes more difficult with elapsed time from gas adsorption, and, the larger, and therefore more serious the defect, the greater is the likelihood that it will not be detected.

It is an object of this invention to improve upon the Eddy process, and, more specifically, it is an object to provide an improved process for nondestructively testing with adsorbed radioactive gas, which process is capable of more effectively immobilizing the gas in or adjacent surface voids. Further, it is an object to reduce the time dependency of the process and to increase its reliability in detecting larger surface voids.

This invention in one aspect relates to a method of nondestructively testing an article surface for substantially invisible voids comprising adsorbing a radioactive gas on the surface of the article by bringing it into contact with the gas. The adsorbed gas is disproportionately retained on those surfaces presented by the substantially invisible voids as compared to the remaining surfaces of the article contacted by the radioactive gas. Radiation released by the radioactive gas remaining adsorbed is utilized to identify the substantially invisible voids. In this method my improvement is comprised of providing a sealant composition capable of being chill set. I relate the temperature of the article surface to be tested and the sealant composition so that the article surface to be tested is at a temperature below the chill set temperature of the sealant composition and the sealant composition is at a temperature above its chill set temperature. I then coat the article portion to be tested with sealant composition to form a chill set coating thereon of substantial uniformity.

My invention may be better appreciated by reference to the following detailed description considered in combination with the drawings, in which the figures are sectional schematic diagrams of a highly enlarged arti-

cle portion together with the radioactive gas and coatings associated therewith and, in which

FIG. 1 illustrates the article portion after radioactive gas has been adsorbed onto its surfaces and after most of the radioactive gas has been desorbed from the surfaces other than that presented by the surface void;

FIG. 2 illustrates the article portion after being coated in a conventional manner so that the radioactive gas has not been immobilized within the surface void; and

FIG. 3 illustrates the article portion after being coated with a sealant layer according to my invention.

The present invention relates to nondestructive testing using radioactive gases. While this invention is generally applicable to the use of radioactive gases, I prefer to employ those radioactive gases which exhibit an extended half-life—i.e., more than a day—since this avoids the necessity of forming the gas immediately before use and further avoids high initial radiation levels. The radioactive gas can emit alpha, beta and/or gamma radiation. I prefer to employ radioactive gases which emit radiation that is readily attenuated in the atmosphere, such as beta radiation, so that the need for shielding is minimized. I further prefer to use radioactive gases that are relatively inert chemically.

Radioactive krypton—e.g., the radioactive isotope krypton-85—is particularly well suited for use in the practice of this invention. This particular gas is well suited for use in the present invention because of its relatively small atomic diameter, 3 angstroms, a 10 year half-life, and emission of 662 KeV beta and 517 KeV gamma radiation. This particular radioisotope has a branching ratio of 0.46 percent, that is, it emits 46 gammas for each 1,000 betas. Moreover, of the radioactive inert gases, it is readily available. Its inertness is a particularly desirable quality both from the standpoint of nondestructive testing and health, since it does not readily react chemically so as to be chemically bound to tissue or on materials to which it is adsorbed.

The present invention is applicable to the nondestructive testing of articles or article portions for surface voids. The term "surface voids" is defined to include any spatial vacancy, such as a crack, hole, fissure, discontinuity, or the like, which extends beneath the surface of the article and which is at least partially penetrable from the surface. The surface void can open progressively toward the surface, as in an open crack, or can be constricted at its interface with the surface. The geometrical configurations of the surface voids detectable with my process can take a variety of diverse forms.

My process is particularly well suited to the detection of surface voids which are substantially invisible—that is, surface voids which are not readily detected by the naked eye upon purposeful scrutiny. In fact, my process is capable of detecting surface voids of exceptionally small size and is limited only by the molecular dimensions of the gas employed. My process has particular advantage, however, as applied to those surface voids which, although they are so small as to be substantially invisible, are nevertheless large enough to permit the desorption of gas with the passage of time.

For example, in using radioactive krypton it is theoretically possible to cause adsorption which provides detectable surface concentrations in voids of about 10 angstroms in width and larger. Krypton-85, however, is usually supplied as a mixture of 5 percent krypton-85

in krypton-84, and thus, the theoretical sensitivity can be approached only by using pure krypton-85. Nevertheless, with the readily commercially available mixtures of krypton-84 and krypton-85, surface voids of only a few nanometers in width can be detected.

The article or article portions to be tested for surface voids according to my process can be formed of any material on which gas can be adsorbed and desorbed. In order to avoid residual radioactivity I prefer not to test articles or article portions with my process which permanently absorb large quantities of radioactive gas. However, it is recognized that most materials adsorbing radioactive gas will to some extent also absorb the gas. It is preferred to utilize materials wherein absorption is small as compared to adsorption. This is recognized to be a function not only of the material chosen for testing, but also the procedures employed in bringing the material and gas together. I have found my process to be particularly well suited to the testing of structural metals. I specifically contemplate the applicability of my process to ferrous metals, carbon, copper and alloys thereof, noble metals and refractory metals. The non-destructive testing of insulative inorganic materials, such as glass and ceramic materials is also contemplated. My process is particularly suited for the non-destructive testing of articles of all sizes and geometries that can be readily inspected on one or more surface portions by eye or with the aid of optical instruments. My process is particularly applicable to materials that provide intricate or irregular shapes and which exhibit surfaces of high curvature radius.

Any conventional method for adsorbing radioactive gas on the surface to be tested can be employed in the practice of this invention. One preferred approach is to first remove ambient gas which may be adsorbed on the surface to be tested. This can be achieved by reducing the ambient pressure adjacent this surface, as, for example, by placing the article to be tested in a vacuum chamber. After desorption of ambient gas, it is merely necessary to bring the radioactive gas into contact with the surface in order to achieve adsorption. Where the article surface is of uniform composition and is uniformly physically acted upon, the radioactive gas is adsorbed on the exposed surfaces relatively uniformly. It is recognized that the use of moderate pressures can have the effect of removing ambient gas and achieving adsorption of radioactive gas in a single step. Pressures of 1 or more atmospheres above ambient achieve radioactive gas adsorption quite readily. Adsorption of radioactive gas can also be facilitated by employing moderately elevated temperatures, typically less than about 30°C. It is generally preferred not to employ significantly elevated temperatures or pressures, since absorption of radioactive gases is increasingly favored with increases in these parameters. Ion bombardment of the surface to be tested is also useful in dislodging nonradioactive gas which is initially adsorbed.

The next step is to uniformly desorb radioactive gas from those surfaces of the article being tested other than those surfaces presented by the surface void. To accomplish this it is merely necessary to allow the radioactive gas to diffuse. Within a few minutes disproportionation of concentration levels of adsorbed gas occurs. This is because the article surface typically presents an open diffusion path for the adsorbed gas while the surface void, because of its small size, offers a considerably more restricted diffusion path for adsorbed

gas. Further, the surface to area ratio of random voids and particularly cracks tends to be much higher than that of purposefully formed surfaces. Still further, the surface void tends to be shielded from convection currents that promote desorption.

According to the Eddy process it is necessary to move more quickly from gas adsorption to surface examination in order to detect surface defects, since the surface radiation count drops by half in 8 to 9 hours. The radiation drop is more significant with respect to larger surface voids sought to be located than for smaller surface voids. Since Eddy employs krypton as a radioactive gas, the decrease of the radiation count is almost entirely a function of the desorption rather than its half-life.

FIG. 1 schematically illustrates a detail of an article portion 1 comprised of a base portion 3 and a surface layer 5 containing a surface void 7. The surface void is shown in the form of a crack in the base portion and as a somewhat constricted opening 9 in the surface layer. Molecules 11 of radioactive gas are shown as they might be distributed after adsorption on the surface of the article portion followed by desorption from those article surface portions other than those presented by the surface void. Some molecules are shown diffusing from the surface void, some diffusing within the surface void and some adsorbed within the base portion and surface layer of the article portion.

Eddy has suggested the use of white paint followed by dipping in a photographic emulsion as a way of detecting surface voids for articles exhibiting a complex shape. Unfortunately, paints and emulsions form coatings of irregular thickness on parts of irregular shape. The consequence of attempting to apply a coating to the article portion 1 is clearly illustrated by reference to FIG. 2. A coating 13 is shown applied to the surface to be tested. The coating progressively decreases in thickness as the radius of curvature increases. Since the surface void 7 lies at or near the point of maximum radius of curvature, the coating does not provide an effective barrier to diffusion of the adsorbed gas from the surface void. It can be seen that the few molecules of radioactive gas remaining associated with the article portion and the coating are more or less randomly distributed so that it would be difficult, if not impossible, to detect the presence, size or location of the surface void merely by sensing an areal differential in radiation emissions.

I have improved upon the Eddy process by discovering a technique for immobilizing radioactive gas at the location of the surface void. My technique is well suited for use with the larger, more seriously objectionable surface voids and is particularly and unexpectedly advantageous in detecting, locating and characterizing surface voids associated with a high curvature radius surface portion.

My invention contemplates the application of a substantially uniform sealant coating to a surface to be non-destructively tested for surface voids. I have found that this can be readily and advantageously accomplished by relating the temperatures of the article surface to be tested and the sealant composition so that the article surface is at a temperature below the chill set temperature of the sealant and the sealant composition is at a temperature above its chill set temperature. When the sealant composition and the article are then brought together a uniform temperature differential is

present between all contacted surfaces of the article and the sealant composition. The portion of the sealant lying adjacent the article surfaces is then cooled at a uniform rate and as a function of its distance from the surface of the article. It is then apparent that isothermal zones will be generated which concentrically surround the article surface brought into contact with the sealant composition and that, as the sealant composition is cooled by the article, a zone corresponding to or below the chill set temperature of the sealant composition will irradiate outwardly from the contacted article surfaces. Sealant lying within this zone forms a chill set coating of substantially uniform thickness. The thickness of the coating can be readily controlled as either a function of the initial article temperature, as a function of the duration of unset sealant composition-article contact, or by restricting the availability of sealant for setting. In a preferred form the sealant is rapidly, preferably substantially instantaneously, chill set on the article surface. This is achieved by adjusting the relative article and sealant composition temperatures so that the article is at a temperature of at least 5°C below the chill set temperature of the sealant. In most instances it is desired to cool the article to a temperature substantially below the chill set temperature of the sealant. This is typically at least 20° C below the chill set temperature. It is, of course, not essential that the article to be tested be cooled at all. By proper choice of sealant compositions it may be more convenient to heat the sealant composition to a temperature above ambient and sufficiently above its chill set temperature to establish the desired temperature differential. The chill set temperature can be chosen so that it is above or below the ambient temperature.

A number of manipulative procedures can be employed for forming the chill set sealant coating. In a simple, preferred procedure the article is simply dipped into the sealant composition and removed when the desired coating thickness is achieved by chill setting. In an alternate technique the sealant composition can be sprayed onto the article surface to be coated until the desired coating thickness is obtained. In most instances the chill set sealant coating will be quite thin, typically less than a millimeter and most typically below about 500 microns. Such coating thicknesses are readily obtained in a substantially instantaneous manner. If it is desired to build up sealant coatings of very substantial thickness this can usually be accomplished in a single coating step. In some instances it may be desired to form multiple coatings either for the purpose of altering the composition from layer to layer or to achieve greater thicknesses. For example, where the sealant composition is a poor thermal conductor, it may be desirable to first form a coating and then to allow the coating to reach thermal equilibrium with the article before forming an additional coating. In this manner very thick coatings can be formed while any tendency toward nonuniformity is minimized.

The advantage of my invention is illustrated in FIG. 3. In this figure the article portion 1 is taken in the condition shown in FIG. 1 and a sealant coating 15 is chill set on the surface. The sealant coating is of substantially uniform thickness. It can be seen that while some radioactive gas molecules are absorbed within the article portion and some randomly scattered molecules are desorbed into the sealant coating, the majority of the radioactive gas molecules are retained within or adja-

cent the surface void sought to be detected. Thus, the surface void is very readily detected even though it is comparatively large and at a point of high curvature radius.

The sealant composition can be applied in the form of an emulsion, latex or dispersion, for example, incorporating the sealant. The sealant can take the form of any viscous or solidifiable material which will immobilize the radioactive gas. Natural and synthetic polymers are readily employed as sealants in combination with a solvent or liquid dispersant. While the sealant and its dispersant or solvent can be used in widely varied proportions, the sealant is typically employed in concentrations of from about 5 to 95 percent by weight based on total weight. Instead of being diluted with a solvent or dispersant, the sealant can be used along in a liquid state. For example, the sealant can be applied in a molten state and chill set on the article being tested. Exemplary preferred sealants include polyvinyl alcohol, polyvinylidene chloride, polyvinyl acetals (e.g., polyvinyl butyral), polyalkylenes (e.g., polyethylene, polypropylene, etc.), polyhaloalkylenes (e.g., polyvinylidene fluoride) and more specifically polyperfluoroalkylenes (e.g., polytetrafluoroethylene, polyhexafluoropropylene), polyamides, collodion, cellulose, gelatin, etc.

The solvent or dispersant can take any convenient form, but is preferably chosen to be readily volatilized so as to leave behind a residual sealant coating. Volatilization is preferably accomplished under conditions of temperature and humidity that minimize surface hardening of the sealant so that large amounts of solvent or dispersant are not occluded by the sealant coating. Typical solvents and dispersants include water, tetrahydrofuran, alcohols (e.g., methanol, ethanol, propanol, etc.), ketones (e.g., acetone, etc.), aldehydes (e.g. acetaldehyde, etc.), volatile hydrocarbons (e.g., butane, pentane, octane, etc.), amides (e.g., dimethylformamide, etc.), and other well known volatilizable solvents.

The sealant need not itself be capable of producing an image or alterable in any way by the radioactive gas; however, the sealants are not limited to nonradiation-sensitive materials. Sealants can be employed which are capable of imaging or of alteration by radiation released by the trapped radioactive gas or from radiation from other sources. For example, a photoresist composition can be employed as a sealant which is permanently set in place after initial chill setting by exposure to light or other radiation. Such photoresists can be formed from any conventional photopolymerizable or photocrosslinkable material. Heat setting of sealants, as by heat induced crosslinking, after chill setting is specifically contemplated.

The sealant layer can itself produce an image corresponding to the void, crack or discontinuity which has adsorbed the radioactive gas, provided the sealant is chosen to be a radiation-responsive material or is employed in combination with such a material. The specific choice of radiation-responsive materials is a function of the type and intensity of radiation released by the adsorbed gas of the duration of exposure contemplated. Generally it is preferred to utilize radiation-responsive materials which are capable of image amplification—that is, capable of altering many molecules of imaging material in response to a single unit of radiation. Polyacetylenic materials are exemplary of con-

ventional non-silver imaging materials capable of image amplification.

Conventional silver halide emulsions and dispersions are specifically contemplated to be useful as sealants in the practice of this invention. Silver halides are particularly desirable image-recording materials, since they exhibit amplification properties which exceed the amplification capabilities of nonsilver imaging systems useful as sealants. Useful silver halides include silver chloride, silver chlorobromide, silver iodide, silver chloriodide, silver bromiodide and silver chlorobromiodide. It is specifically preferred to employ silver iodides because of their comparatively high speed. It is also preferred to use silver halide grains of comparatively large size, typically above 0.5 microns, since speed increases with increasing grain size. The larger the grain size the greater the probability of the grain being struck by emitted radiation. Suitable large grain, fast emulsions and dispersions are conventionally employed in forming radiation-responsive elements for X-ray applications.

The silver halide emulsions and dispersions can comprise, for example, silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide crystals or mixtures thereof. The emulsions can be coarse or fine grain emulsions and can be prepared by a variety of techniques, e.g., single jet emulsions such as those described in Trivelli and Smith, *The Photographic Journal*, Vol. LXXIX, May, 1939 (pp 330-338), double jet emulsions such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264 issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 16, 1967 and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. Silver halide emulsions can form latent images predominantly on the surface of the silver halide grains, or predominantly on the interior of the silver halide grains such as those described in Davey et al. U.S. Pat. No. 2,592,250 issued May 8, 1952; Porter et al. U.S. Pat. No. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968 and Bacon et al. U.S. Pat. No. 3,447,927 issued June 3, 1969. If desired, mixture of such surface and internal image-forming emulsions can be made, such being described in Luckey et al U.S. Pat. No. 2,996,382 issued Aug. 15, 1961. Silver halide emulsions can be regular grain emulsions such as the type described in Klein and Moisar, *J Phot. Sci.*, Vol. 12, No. 5, September/October, 1964, pp 242-251 and German Pat. No. 2,107,118. Negative type emulsions can be made, as well as direct positive emulsions as described in Leermakers U.S. Pat. No. 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. Pat. No. 2,541,472 issued Feb. 13, 1951; Schouwenaars British Pat. No. 723,019 issued Feb. 2, 1955; Illingsworth et al. French Pat. No. 1,520,821 issued Mar. 4, 1968; Illingsworth U.S. Pat. No. 3,501,307 issued Mar. 17, 1970; Ives U.S. Pat. No. 2,563,785 issued Aug. 7, 1951; Knott et al. U.S. Pat. No. 2,456,953 issued Dec. 21, 1948 and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958.

The silver halide emulsions and dispersions can be sensitized with chemical sensitizers, such as with: reducing; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Procedures for chemically sensitizing silver halide emulsions are described in Sheppard et al. U.S. Pat.

No. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967 and Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967.

Silver halide emulsions and dispersions can contain development modifiers that function as speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. No. 3,046,134 issued July 24, 1962; Carroll et al. U.S. Pat. No. 2,994,900 issued July 12, 1960 and Goffe U.S. Pat. No. 3,294,540 issued Dec. 27, 1966.

The silver halide emulsions and dispersions can be protected against the production of fog (that might be induced by the composition of the article surface being tested or by other materials) and can be stabilized against loss of sensitivity during keeping. Useful anti-foggants and stabilizers, each used alone or in combination, include: a) thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 issued Sept. 27, 1938 and Allen et al. U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; b) the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959 and Heimbach et al. U.S. Pat. No. 2,444,605 issued July 6, 1948; c) the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; d) the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; e) the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; f) the oximes described in Carroll et al. British Pat. No. 623,448 issued May 18, 1949; g) nitron; h) nitroindazoles; i) the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897 issued Aug. 16, 1966; and Luckey et al. U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; j) the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; k) the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; and l) the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 issued Aug. 28, 1951; and Yutzy et al. U.S. Pat. No. 2,597,915 issued May 27, 1952.

Photographic silver halide sealant layers can contain various sealants alone or in combination as vehicles. Suitable hydrophilic vehicle materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

Photographic sealant layers can contain alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric vehicle compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Typical synthetic polymers include those described in Nottorf U.S. Pat. No. 3,142,568 issued July 28, 1964; White U.S. Pat. No. 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat. No. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S. Pat. No. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. No. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. No. 3,411,911 issued Nov. 19, 1968. Other vehicle materials include those water-

insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing as described in Smith U.S. Pat. No. 3,488,708 issued Jan. 6, 1970, and those having recurring sulfobentaine units as described in Dykstra Canadian Pat. No. 774,054.

The photographic sealant layers can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton et al U.S. Pat. No. 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robijns U.S. Pat. No. 2,588,765 issued Apr. 11, 1952 and Duane U.S. Pat. No. 3,121,060 issued Feb. 11, 1964; and silicone resins such as those described in DuPont British Pat. No. 955,061 issued Apr. 15, 1964.

The photographic sealant layers can contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. No. 2,600,831 issued June 17, 1952; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. No. 3,133,816 issued May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. No. 1,022,878 issued Mar. 16, 1966; and Knox U.S. Pat. No. 3,514,293 issued May 26, 1970.

Since many surfaces offer poor visual contrast with the radiation-induced image, it is contemplated that a pigment or dye can be incorporated into the sealant layer. While the temperature of the article and the sealant composition can be related to control the thickness of the sealant coating, because of the desire for near-instantaneous chill setting to occur, it can in some instances be desirable to build up coatings somewhat thicker than actually required for image-recording purposes. The use of pigments—particularly white pigments, such as titanium dioxide—is a means of reducing the effective photographic thickness of a sealant coating. The titanium dioxide effectively masks any background printout attributable to lack of fixation of the inner portions of the sealant layer.

In a number of applications it can be desirable to stir the sealant composition prior to coating. This can lead to the entrapment of air bubbles where mechanical stirring is employed. It has been discovered that the incorporation of a thickening material within the sealant composition, such as hydroxyethylcellulose added to a silver halide in gelatin dispersion, can significantly reduce the entrapment of air bubbles. Preferably a thickening agent and a surfactant are employed in combination for this purpose.

As is well appreciated by those skilled in the art, panchromatic sealant compositions must be prepared and used in the dark while sealant compositions lacking sensitivity to the longer wavelength portions of the electromagnetic spectrum can be prepared and used under safelight conditions, but cannot be exposed to daylight if a useful radiation-induced image is to be obtained. It is my recognition that the sealant layer can be desensitized to ambient light—i.e., daylight—while retaining its sensitivity to radiation emitted by adsorbed radioactive gas. This is possible since light exhibits an energy level of only 3 electron volts while radioactive gases typically emit much more energetic radiation. For example, the beta particles emitted by radioactive krypton typically exhibit an energy level of approximately one-half million electron volts. Silver halide de-

sensitizers are well known in the art. Silver halide emulsions and dispersions are also known in the art that are selective to low or intermediate levels of radiation. Such sealants can be used to advantage to record soft radiation, that is, radiation in the form of a gamma ray or a beta particle that has already undergone one or more atomic collisions, as would be typically received from a surface void, as contrasted to hard radiation, that is, radiation in the form of a gamma ray or beta particle that comes directly from the article surface to the sealant layer without or with fewer intervening atomic collisions.

Where the sealant layer is not itself a radiation-responsive layer that is capable of forming a visible or latent image, the sealant layer acts to immobilize the adsorbed radioactive gas while separate layer or means must be employed to detect the radiation emitted by the adsorbed radioactive gas. This can take the form of any one of the radiation-detection approaches disclosed in the Eddy patent, cited above. In a simple form conventional radiation-sensitive recording elements can be physically positioned over the sealant coating and held in position for a length of time sufficient to achieve exposure. It is also contemplated that a second sealant layer which is in this instance a radiation-sensitive recording material such as a silver halide emulsion or dispersion, overlies the first sealant layer. A subbing layer can be disposed between the two subbing layers. Subbing layers are well known in the photographic arts for facilitating the coating of a hydrophilic radiation-responsive layer onto a hydrophobic surface. It is specifically contemplated that the first sealant layer can take the form of a conventional photographic subbing composition. Instead of employing a separate subbing layer the first sealant layer can be chemically treated or mechanically textured to bond the second sealant layer. The first sealant layer where it is chosen to be nonradiation-responsive can be identical in composition to a silver halide emulsion or dispersion, but lack radiation-responsive silver halide. The first sealant layer in addition to its sealant function can also perform the valuable function of protecting the second, radiation-responsive sealant layer from desensitizing contaminants associated with the article surface. While two layers are discussed above, it is recognized that the sealant layers can be further multiplied without detracting from their intended function. It is preferred that all of the sealant layers be chill set according to the procedure of this invention; however, it is recognized that this is not essential. In most instances, at least the first applied sealant layer is chill set according to the practice of this invention.

In many instances a photographic image will print out directly on the object being tested without any processing whatsoever. In other instances processing of a conventional type will be required to produce a visible image that is not destroyed upon viewing in ambient lighting. In most instances, it will be convenient to process the object to be tested with radiation-responsive material located directly thereon. This avoids having to correlate the object with a photographic record of any void, crack or discontinuity contained therein. In other instances, as where a conventional photographic element is employed for imaging, it may be convenient to remove the element for processing separate from the object being tested. In still other instances it may be convenient to strip the sealant layer or a radiation-

responsive imaging layer overlying the sealant layer (which, of course, may also be a sealant layer) from the object for the purposes of separate processing. Separate processing may be convenient where the composition of the object or some part thereof would tend to contaminate the processing materials being used for image development. The dispersion, after processing on the article, can be easily removed mechanically or chemically. For example, it is well known to strip silver halide gelatin coatings with alkali. To avoid chemical attack on the article a gelatinase enzyme has been found to be quite effective stripping agent.

The following specific embodiments are set forth to further illustrate the practice of this invention:

Gas containing krypton-85 was introduced into surface imperfections of jet engine turbine blades by the following means: The blades were placed in a vacuum system (commercially available as a Norton Vacuum system, Model 3117) which is capable of pumping below  $10^{-3}$  torr. After the pressure of the bell jar of the vacuum system was reduced below  $10^{-3}$  torr., the pumping system was sealed off from the bell jar and a gas containing krypton-85 was bled in until the pressure was only slightly less than atmospheric pressure. A high speed pumping system was then used to remove the krypton-85 gas. The pump was sealed off and the inside of the bell jar was quickly brought to atmospheric pressure by opening it to room air. The turbine blades were immediately removed from the bell jar and coated with approximately 25 microns (dry thickness) of polyvinyl alcohol by the following method: A 5 percent solution of polyvinyl alcohol in water was applied to the turbine blade by dipping the turbine blade into the sealant composition. The turbine blade was cooled to approximately  $0^{\circ}\text{C}$  in liquid nitrogen prior to dipping. The turbine blades were dipped and removed in a continuous manual movement. The polyvinyl alcohol instantaneous chill set as a substantially uniform coating on all surfaces of the turbine blades brought into contact with the sealant composition. The coating was noted to extend around the edge of the turbine blades without any visible thinning.

An ordinary coarse-grained silver bromiodide in gelatin dispersion of the type used in radiography was chemically sensitized to its optimum speed. To this dispersion was added 30.7 mg of bis(4-morpholiniothiocarbonyl)disulfide per silver mole and 5.3 mg of 1,3-diamino-5-methyl phenazinium chloride per silver mole to render the dispersion selectively sensitive to soft beta and gamma radiation as opposed to hard beta or gamma radiation.

The sealed turbine blades were then coated with the radiation-sensitive dispersion with the gelatin held at a temperature of  $30^{\circ}\text{C}$ . After coating with polyvinyl alcohol and silver halide dispersion the turbine blades were held in the dark for 4 hours. The blades were then, while still in the dark, immersed in a tank of a methyl-p-aminophenol sulfatehydroquinone developer (commercially available under the trademark Kodak KRX) at  $20^{\circ}\text{C}$  for 4 minutes, washed in water and fixed in a fixing bath (commercially available under the trademark Kodak F-5)

The turbine blades were examined visually and surface voids were indicated on some of the blades by developed silver marks on the processed dispersion coating. These surface voids were confirmed by sawing through the turbine blade beside the surface void. The

above procedure was repeated omitting the polyvinyl alcohol sealant layer, but identically chill setting the silver bromiodide in gelatin dispersion in its place. A similar methyl-p-aminophenol sulfate-hydroquinone developer (commercially available as under the trademark Kodak Developer D-19) was used. Substantially uniform coatings were again formed with similar effectiveness in detection of surface voids.

Substantially similar results can be achieved by chill setting other polymers sealant coatings in a substantially similar manner. For example, polyvinyl butyral and polyvinylidene chloride are similarly useful, although somewhat less effective sealing of adsorbed gas is noted. Sprayed on coatings of polyvinyl alcohol are also noted to be readily chill set. In another form, melted polyethylene can be readily chill set as a substantially uniform coating on the turbine blades.

The procedure described in detail above using polyvinyl alcohol sealant composition and dipping the turbine blades into this sealant composition was repeated, but gelatin layers containing 20 percent by weight of the phosphor zinc sulfide were interposed between the first and second sealant layers. In another procedure 20 percent by weight calcium tungstate was added to the radiation-responsive silver halide dispersion.

While my invention has been disclosed with reference to certain preferred embodiments, it is recognized that numerous variations will readily occur to those having ordinary skill in the art. It is accordingly intended that the scope of my invention be determined by reference to the following claims.

I claim:

1. In a method of nondestructively testing an article surface for substantially invisible voids comprising

- a. adsorbing a radioactive gas on the surface of the article by bringing it into contact with the gas,
- b. disproportionately retaining the adsorbed radioactive gas on those surfaces presented by the substantially invisible voids as compared to the remaining surfaces of the article contacted by the radioactive gas, and
- c. utilizing radiation released by the radio-active gas remaining adsorbed to identify the substantially invisible voids,

the improvement comprising

1. providing a sealant composition capable of being chill set,
  2. relating the temperatures of the article surface to be tested and the sealant composition so that the article surface to be tested is at a temperature below the chill set temperature of the sealant composition and the sealant composition is at a temperature above its chill set temperature, and
  3. coating the article portion to be tested with sealant composition to form a chill set coating thereon of substantially uniform thickness.
2. In a method according to claim 1 the further improvement in which the article surface is cooled to a temperature below ambient to achieve chill setting.
3. In a method according to claim 2 the further improvement in which the article surface is cooled to a temperature at least  $5^{\circ}\text{C}$  below the chill setting temperature.
4. In a method according to claim 3 the further improvement in which the article surface is cooled to a temperature at least  $20^{\circ}\text{C}$  below the chill setting temperature.



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5. In a method according to claim 1 the further improvement in which the chill set sealant coating is over-coated with a radiation-responsive, imaging and sealant layer.

6. In a method according to claim 5 the further improvement of associating a phosphor with the over-coated sealant layer.

7. In a method according to claim 5 the further improvement in which a third sealant layer is interposed between the chill set sealant layer and the radiation-responsive sealant layer.

8. In a method according to claim 7 the further improvement in which a phosphor is incorporated into the interposed sealant layer.

9. In a method according to claim 1 the further improvement in which said sealant composition contains a photographic silver halide.

10. In a method of nondestructively testing an article surface for substantially invisible voids comprising

- a. adsorbing a radioactive gas on the surface of the article by bringing it into contact with the gas,
- b. disproportionately retaining the adsorbed radioac-

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tive gas on those surfaces presented by the substantially invisible voids as compared to the remaining surfaces of the article contacted by the radioactive gas, and

c. utilizing radiation released by the radioactive gas remaining adsorbed to identify the substantially invisible voids,

the improvement comprising

1. providing a sealant composition capable of being chill set and incapable of producing an image upon exposure to radiation,

2. relating the temperatures of the article surface to be tested and the sealant composition so that the article surface to be tested is at a temperature below the chill set temperature of the sealant composition and the sealant composition is at a temperature above its chill set temperature, and

3. coating the article portion to be tested with sealant composition to form a chill set coating thereon of substantially uniform thickness.

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