Nov. 30, 1965 E. C. YACKEL ETAL 3,220,840

INFLATABLE PHOTOGRAPHIC ELEMENTS INCLUDING AN ELASTIC SILVER HALIDE EMULSION, AND PROCESS FOR MAKING SAME

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Fig. 1

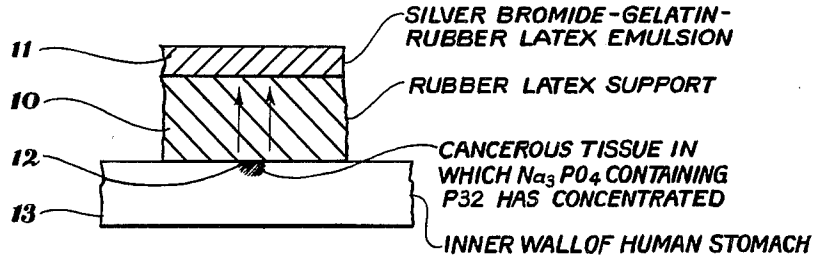


Fig. 2

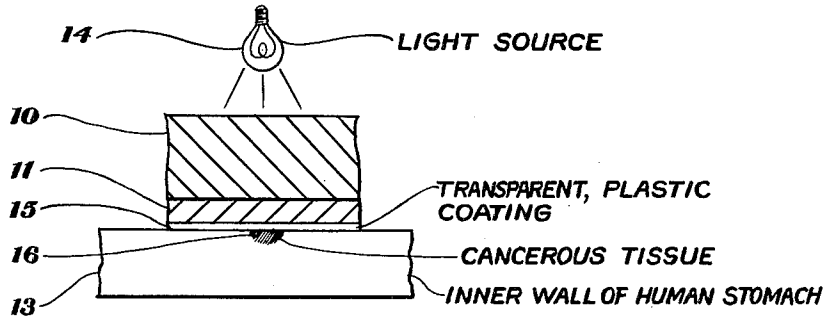
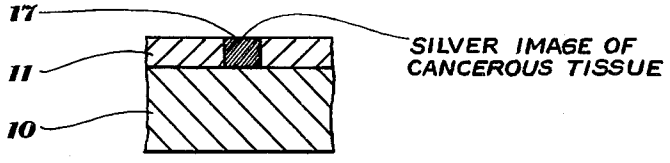


Fig. 3



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Fig. 4

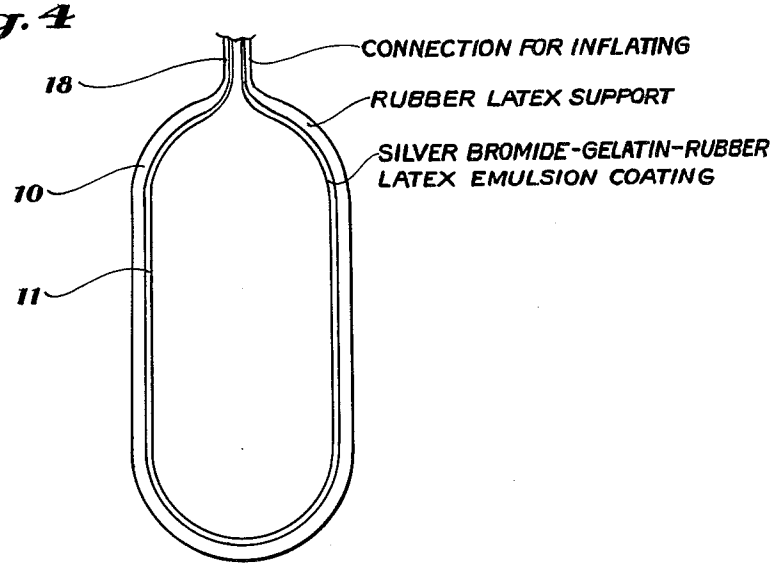


Fig. 5

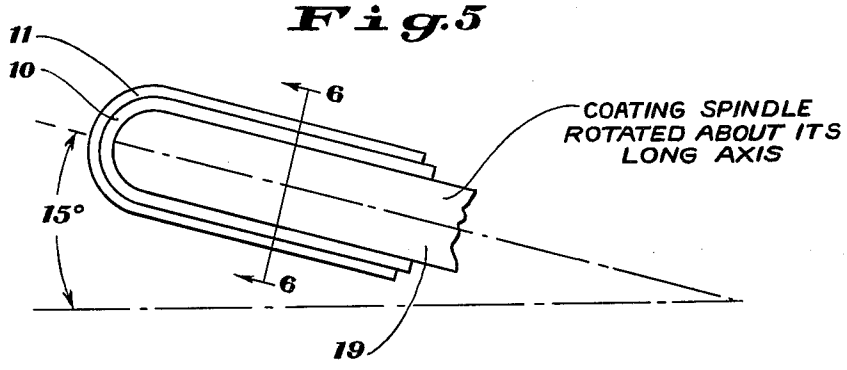
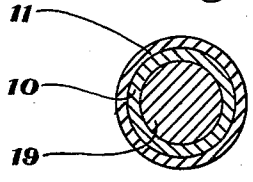


Fig. 6



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INFLATABLE PHOTOGRAPHIC ELEMENTS INCLUDING AN ELASTIC SILVER HALIDE EMULSION, AND PROCESS FOR MAKING SAME

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This invention relates to photographic elements and more specifically to stretchable, radiation-sensitive elements adapted for use in photographing the inside walls of various organs in the living human body.

The two methods that have been attempted for photographing the inside walls of an organ, such as the stomach, inside the live human body are (1) photography through a gastroscope and (2) the use of tiny cameras lowered into the stomach together with suitable illuminating means. Although the first method has met with some success, it cannot be used as a routine diagnostic procedure owing to the loss of light in the long periscopic instrument and the low illumination available as well as to the unsharpness and small field of view. The second method, involving the use of tiny cameras, has not proved at all successful so far.

Heretofore there has not been a simple method available for routinely photographing the inner surface of the human stomach or other internal organs for early positive diagnosis of pathological conditions.

It is, therefore, an object of our invention to provide a photographic element for use in a relatively simple and easy method for photographing the inside walls of various organs in the living human body for the routine detection of pathological conditions.

Another object is to provide a novel, stretchable, radiation-sensitive element especially adapted for use in photographing the inside walls of various organs in the living human body.

Another object is to provide a hollow, inflatable, radiation-sensitive element which, when deflated, can be placed inside the cavity formed by an organ, such as the stomach, inside a live human body; then inflated to press the radiation-sensitive element gently against the interior walls of the cavity, exposed to produce a latent image in the radiation-sensitive emulsion, then deflated, removed, and the latent image developed to produce a permanent visible image of the cavity walls for pathological study.

Another object is to provide a silver halide sensitized element, which may be stretched extensively before, during, and after exposure and processing, and which if permitted will again return to its normal dimensions.

Another object is to provide a method for making the hollow, inflatable, radiation-sensitive element suitable for use in making pathological studies of the internal cavity walls of organs in a living human or animal body, or for use in the study of cavity walls in metal formations.

Other objects will be apparent from the following specification and claims.

We have found that the above objects and other objects can be accomplished by using the silver halide sensitized, stretchable photographic elements of our invention. In its simplest form, the element of our invention consists of a thin, elastic balloon, over which is coated a flexible, radiation-sensitive emulsion layer, containing silver halide and a water-permeable, hydrophilic colloid, e.g., gelatin, albumin, etc.

These elements are made by using an elastic support such as a thin layer of natural rubber latex, synthetic rubber latex, or any other plastic which has elastic properties. The elastic material can be treated with a coating aid, such as a solution of saponin, then coated with a silver halide emulsion, containing, for example, gelatin and a dispersion of rubber latex, such as a Lotol dispersion, to increase flexibility.

In the preferred form, the photographic element of our invention is made in the shape of a bag, balloon, or hollow, inflatable, sausage-shaped element, which collapes into a very small compass, which need be no greater in size than that of a thin, flexible piece of cord, which upon inflation with air, other innocuous gases, or fluids takes up and conforms to the shape of the stomach (or other organ being studied) and is pressed against its walls at all times during exposure. A thin rubber tube is attached to the bag for inflating it and also to aid in removing the exposed and deflated element from the stomach. The tube may be attached at one end only of the bag or at both ends, so as to pass through the bag's length thereby facilitating the insertion through the stomach to the pyloric opening. The device can even be used to penetrate beyond the pyloric opening or into the duodenum so as to photograph the lining in those areas. The device is also used for exploring the lining of the uterus, rectum, sigmoid, and colon in order to supplement the usual methods of investigation in those regions.

The emulsion coated on our element can advantageously be sensitized with silver halide or mixed silver halides, such as silver bromide, silver chloride, silver chlorobromide, silver bromoiodide, etc. Any gelatin suitable for photographic purposes may be used. The elastic material used to give our emulsion layers their elastic properties can advantageously be any rubber latex dispersion in water, such at Lotol, Lotol 638, Lotol NC–356, Lotol B, etc., manufactured by the Naugatuch Chemical Company, a division of the U.S. Rubber Company or styrene-butadiene copolymers such as are sold under the trade name, Buna-S by Goodrich Rubber Company. Some rubber latexes contain photographically active sulfur compounds as vulcanizing agents. Since sulfur compounds of this type usually cause fog and other deleterious effects in photographic emulsions, it is preferably to use for both support and the emulsion a rubber latex containing no photographically active sulfur compounds as vulcanizing agents. When natural rubber balloons are used, the best adhesion can be obtained by using natural rubber latex in the emulsion layer. However, when synthetic rubber balloons are used better results usually are obtained by using synthetic rubber latex in the emulsion layer.

Although various mixtures of the rubber latex and hydrophilic colloid are used in the emulsion, we have found that the preferred composition contains from 80 to 90 percent rubber latex and from 10 to 20 percent hydrophilic colloid.

The physical requirements for the emulsion coating are similar to those for the support which may be in the form of a sheet or balloon described previously. However, in addition to these requirements the stretching and crinkling, which the photographic element is subjected to during its use, must not detach the emulsion coating from the support or leave pressure marks in the final image. The photographic qualities required of the emulsion will depend upon the method of illumination adopted for exposing the elements. For flash or tungsten lighting any of the emulsion types usually employed in clinical photography are suitable; for fluorescent or X-ray (or radium) methods of illumination, X-ray types of emulsion are employed, and with infra-red lighting, infra-red sensitized emulsions are used.

The emulsion is applied most advantageously to the outer surface of the rubber balloon. However, in use, the balloon made in this manner may be turned inside out so

that the radiation-sensitive emulsion layer is on the inside of the balloon. When the element is to be used with the emulsion layer on the outside of the balloon, it is usually advantageous to coat the emulsion layer with a transparent, flexible, protective coating, which is impervious to the stomach (or other body) fluids but which can be readily removed after exposure and before the latent image is developed to a silver image. When the balloon is arranged so that the senitive emulsion layer is on the inside, there is no need for such a protective coating.

Since the radiation-sensitive emulsion of our element is generally sensitive to light, its insertion and removal from the stomach of the patient being examined must be done in a darkened room. Opaque coatings can be made over the outside of the sensitized balloon so that insertion of the balloon can be accomplished in the light. However, such coatings must be removable in the stomach before exposure when light is used for making the exposure. If the exposing radiation is not visible light but infra-red, X-ray, or radiation from radoactive material, such an opaque coating, if it transmits the radiation used for the photography, can be left on during the exposure and need not be removed until the developed image has been fixed and is ready for viewing, provided that it does not impede access of the processing chemicals to the photographic layer.

The following examples will serve to illustrate the preparation of a typical silver halide sensitized, stretchable photographic element.

Example I

A concentrated silver halide emulsion was prepared, which contained 20 g. of precipitated silver bromide, 5 g. of gelatin in 100 cc. of water, and was free of all but traces of potassium nitrate and potassium bromide. One part of this mixture was mixed with an equal part of Lotol rubber latex in water (50 percent solids). This in turn was diluted with two parts of water and then coated thinly over about 30 sq. ft. of a clean piece of rubber sheeting and permitted to dry. When dry, the material was found to adhere to the rubber sheeting during stretching as much as three to five times. This material was exposed and processed in a normal manner with the exception that developing and fixing times were extended from two to three times normal, depending upon the thickness of the emulsion coating. It was found that stretching and restretching of the element could be repeated without harm to the coated material or the image produced upon exposure and development of the material.

The following examples will serve to illustrate how typical, hollow, inflatable, radiation-sensitive elements of our invention are made.

Example II

A natural rubber latex balloon was slipped over a 38 by 200 mm. Pyrex test tube, which was dusted with finely ground talc powder. After being slipped smoothly on the test tube, the balloon was swabbed with a pledget of cotton dipped in a dilute solution of saponin. Following the swabbing treatment, the balloon was rinsed with distilled water and dried. The treated base, or support, was then dip-coated in the following emulsion.

To a fine grain silver bromide emulsion weighing 400 g. per mole of silver bromide and containing 30 g. of gelatin per mole of silver bromide, there was added 240 g. of distilled water, 40 g. of a 10 percent aqueous gelatin solution and 20 cc. of a 5 percent Alkanol B (a propylated naphthalene sulfonate) solution. This mixture was melted at 40° C. and poured with stirring into 200 g. of Lotol brand rubber latex containing 40 percent solids.

After mixing directly by careful stirring, the emulsion was filtered through flannel to remove any bubbles and the temperature adjusted to 29.4° C. The rubber balloon, supported by the Pyrex test tube, was coated by dipping for about 10 seconds in the emulsion and then quickly transferred to the rotating chuck of the coating machine. The chuck was inclined upward at the free end at an angle of 11° and was rotated at a speed of 35 to 40 revolutions per minute. After rotating for about one minute, dry air was forced from a fan to the surface of the coating at a low velocity so that there was no danger of disturbing the liquid emulsion. After approximately four to five minutes, sufficient drying had occurred so that there was no danger of emulsion flowing. At this point the tube was removed from the chuck and supported in a vertical position and allowed to dry completely in still air at a temperature of 23.9° C. and relative humidity of 50 percent.

Example III

To 100 g. of a silver chlorobromide emulsion weighing 1,000 g. per mole of silver bromide and containing 5 g. of gelatin per mole of silver bromide, there was added 100 g. of water, 100 g. of 10 percent gelatin solutions, 20 g. of 5 percent Alkanol B and 200 g. of Lotol rubber latex containing 40 percent solids. These ingredients were mixed together with stirring at 40° C. and the emulsion was coated on the rubber balloon as described in Example II except the coating temperature was 32.2° C. and the inclination of the chuck was 15°.

The coating angle at which the chuck is set depends upon the viscosity of the emulsion and the speed at which the chuck is rotated. It is necessary to adjust these two variables in order to get flow of the liquid emulsion in two directions for even coating. The preferred coating angle of the chuck varies from approximately 5° to 30° from the horizontal.

Various methods can be used for exposing the radiation-sensitive elements of our invention in order to produce the photographic image of the inner walls of the body cavity being studied for pathological conditions.

The principal methods for making the exposure are as follows:

(a) A tiny flash bulb or photoflood lamp can be located inside the transparent bag and the radiation-sensitive emulsion is exposed by reflex printing as is used in certain forms of document copying. A slightly milky fluid can be used to advantage inside the bag as the bag illuminating medium to diffuse and equalize the exposing radiation.

(b) Fluids can be used in the bag, which upon mixing produce the required illumination. These fluids must of course be innocuous in case of rupture of the bag.

(c) A fluorescent or phosphorescent liquid can be used to inflate the bag.

(d) A fluid capable of fluorescence when excited by X-rays or radium can be utilized.

(e) Fluorescent materials can be incorporated in the emulsion or coated separately, and excited by X-rays.

(f) With infra-red-sensitive emulsions protected from rays of other wave lengths, warm water can be used for inflating the bag if sufficient sensitivity can be obtained at the comparatively low temperatures, or air or other innocuous gas can be used for inflating the bag and infra-red lamps used in flash bulb or photoflood form as a source of infra-red radiation.

(g) A solution of a compound such as sodium phosphate containing radioactive phosphorus P_{32} can be applied to the human tissue before exposure is made. For making studies of a stomach, for example, the patient swallows or is injected with a quantity of a solution of the radioactive phosphorus compound just before the sensitized balloon is inserted and inflated. Exposure by the radioactive compound, which concentrates preferentially in cancerous tissues, takes about two to six hours. High density areas produced by development of the exposed element correspond to cancerous tissue.

After exposure, the latent image in the exposed element is developed in any conventional black-and-white developer. Usually these developers contain hydroquinone or a hydroquinone derivative as the developing agent either alone or in combination with some other developing

agent such as p-methylaminophenolsulfate. The following formula is typical of developers useful for developing our exposed elements.

Water	cc	about 500
p-Methylaminophenolsulfate	g	2.0
Sodium sulfite (desiccated)	g	90.0
Hydroquinone	g	8.0
Sodium carbonate (monohydrate)	g	52.2
Potassium bromide	g	5.0

Water to make 1 liter.

The developed image is then fixed with any conventional alkali thiosulfate fixing bath used for photographic purposes.

The accompanying drawings, FIGS. 1, 2, 3, 4, 5, and 6, still further illustrate our invention.

FIG. 1 shows an enlarged cross-sectional view of the radiation-sensitive element comprising the radiation-sensitive, silver bromide-gelatin-rubber latex emulsion layer **11** coated over rubber latex support **10**, which is being exposed by radiation from sodium phosphate containing P_{32}, which has concentrated preferentially in cancerous tissue **12** of the stomach wall **13**.

FIG. 2 shows in an enlarged cross-sectional view how light from light source **14** is being passed through support **10**, sensitized emulsion layer **11**, and transparent, flexible, protective plastic coating **15** to the section of the stomach wall **13** containing cancerous tissue **16** to produce a latent image of the cancerous tissue in emulsion **11**.

In FIG. 3, the latent image produced in emulsion layer **11** by exposure of the element in FIG. 1 has been developed to the silver image **17** of the cancerous tissue.

FIG. 4 shows a cross-sectional view of a partially inflated element comprising a rubber latex balloon with rubber latex support **10** coated with radiation-sensitive layer **11**. Connection **18** is provided for inflating the element.

FIG. 5 shows a cross-sectional view of the rotating spindle **19** upon which is mounted the support **10** that has been dip-coated with emulsion layer **11**. The partially dried, coated element is being rotated with the spindle about its long axis, the free end of which is inclined upward making an angle of 15° with the horizontal plane.

FIG. 6 shows in a sectional view taken from plane **6—6**, the spindle **19**, support **10**, and emulsion layer **11**.

The novel, stretchable, radiation-sensitive elements of our invention are valuable for use in making photographs of the inside walls of body cavities formed by various organs in living human bodies. These elements are characterized by being capable of repeated stretching from three to five times their normal dimensions and then returning to their original shape and size without disturbing the adhesion of the sensitized emulsion to the element support or adversely affecting the emulsion layer either physically or photographically. Furthermore, our stretchable, radiation-sensitive elements can be crinkled and compressed into a small compact package and then returned to their original form without adversely affecting the properties of the emulsion coating. They can be exposed to an image before stretching, in the stretched condition or after stretching. Although our elements are made in various forms, they are particularly valuable when fashioned into hollow, inflatable, sausage-shaped balloons that are used for photographing the inside walls of various organis in the living human body. An important part of our invention is the novel method we have discovered and developed for coating radiation-sensitive emulsions of uniform thickness on the sausage-shaped balloons of our invention.

The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications

can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An inflatable and deflatable elastic radiation-sensitive element comprising a thin walled elastic balloon having coated thereon an elastic radiation-sensitive silver halide emulsion layer containing intimately admixed therein an elastic styrene-butadiene copolymer that is substantially free of photographically active sulfur compounds, such that the said elastic balloon and said elastic emulsion layer cooperate as an integral unit that is adapted for repeated inflation to about five times the coated dimensions of said element, and substantially complete deflation, and is adapted to be turned inside out during use of the element without any separation of the said elastic emulsion coating from the said elastic support.

2. An inflatable and deflatable elastic, radiation-sensitive element comprising a thin walled elastic balloon having coated thereon an elastic radiation-sensitive silver halide emulsion layer containing elastic rubber latex that is substantially free of photographically active sulfur compounds and is intimately admixed in said layer, such that the said elastic balloon and said elastic emulsion layer cooperate as an integral unit that is adapted for repeated inflation to about five times the coated dimensions of said element, and substantially complete deflation, and is adapted to be turned inside out during use of the element without any separation of the said elastic emulsion coating from the said elastic support.

3. An inflatable and substantially completely deflatable elastic radiation-sensitive element comprising a thin walled elastic rubber latex balloon having coated thereon an elastic radiation-sensitive silver halide-gelatin-rubber latex emulsion layer in which the mixtures of said gelatin and said rubber latex in the said emulsion contains from about 10 to about 20 percent gelatin and from about 80 to about 90 percent rubber latex, said rubber latex being elastic and substantially free of photographically active sulfur compounds said rubber latex being intimately admixed in said emulsion layer.

4. An element of claim 3 in which the silver halide is silver bromide.

5. An element of claim 3 in which the silver halide is silver chlorobromide.

6. An element of claim 3 in which the silver halide is silver bromoiodide.

7. An element of claim 3 in which the rubber latex is natural rubber latex.

8. An element of claim 3 in which the rubber latex is synthetic rubber latex.

9. An element of claim 3 in which the said elastic radiation-sensitive silver halide-gelatin-rubber latex emulsion is a developing out emulsion.

10. An inflatable and substantially completely deflatable elastic radiation-sensitive element comprising a thin walled elastic rubber latex balloon having coated thereon an elastic radiation-sensitive silver chlorobromide-gelatin-rubber latex emulsion layer coated from a composition made by intimately mixing 100 g. of water, 100 g. of 10 percent gelatin solution, 20 g. of 5 percent solution of a propylated naphthalene sulfonate solution, 200 g. of rubber latex containing 40 percent solids, with 100 g. of a silver chlorobromide emulsion weighing 1000 g. per mole of silver bromide and containing 5 g. of gelatin per mole of silver bromide, said rubber latex being elastic and substantially free of photographically active sulfur compounds.

11. A process for uniformly coating, setting and drying an elastisc radiation-sensitive silver halide-gelatin-rubber latex emulsion layer on a thin walled elastic balloon support of an elastic radiation-sensitive element comprising the steps:

(1) mounting the said balloon support on a test tube shaped spindle,

(2) coating said mounted support by dipping it in a supply of the liquid silver halide-gelatin-rubber latex emulsion in which the mixture of said gelatin and said rubber latex contains from about 10 to about 20 percent gelatin and from about 80 to about 90 percent rubber latex, said rubber latex being elastic substantially free of photographically active sulfur compounds and intimately admixed in said emulsion,

(3) removing the coated, mounted support from the said supply of liquid emulsion,

(4) rotating the coated mounted support about its long axis at from about 35 to about 40 revolutions per minute with the free end inclined upward at an angle greater than about 5° from the horizontal so that during each complete revolution of the coated support, the flow of the liquid emulsion coating resulting from the force of gravity is reversed and maintains a uniform thickness in said coating until the coating stops flowing, and then

(5) completing the drying of said emulsion layer.

12. A process for uniformly coating, setting and drying an elastic radiation-sensitive silver halide-gelatin-rubber latex emulsion layer on a thin walled elastic balloon support of an elastic radiation-sensitive-element comprising the steps:

(1) mounting the said balloon support on a test tube shaped spindle, having a diameter of about 38 mm.,

(2) coating said mounted support by dipping it in a supply of the liquid silver halide-gelatin-rubber latex in which the mixture of said gelatin and said rubber latex contains from about 10 to about 20 percent gelatin and from about 80 to about 90 percent rubber latex, said rubber latex being elastic, substantially free of photographically active sulfur compounds, and intimately admixed in said emulsion,

(3) removing the coated, mounted support from the said supply of liquid emulsion,

(4) rotating the coated mounted support about its long axis at from about 35 to about 40 revolutions per minute with the free end inclined upward at an angle of from about 5° to 30° from the horizontal to maintain a uniform coating, and

(5) drying on the rotating element until the emulsion coating stops flowing.

13. The process of claim **12** in which the said coated mounted support is rotated for one minute in still air then dried further by passing slow-moving dry air over the rotating element until the emulsion coating stops flowing, and completing the drying process in still air.

14. The process of claim **12** in which the said coated mounted support is rotated for one minute in still air then dried further by passing slow-moving dry air over the rotating element until the emulsion coating stops flowing, and completing the drying process in still air at a temperature of 23.9° C. and a relative humidity of 50 percent.

15. A process for coating an elastic radiation-sensitive emulsion on a hollow, elastic, inflatable support of an elastic radiation-sensitive element comprising the steps of (1) mounting the hollow, inflatable support on a test tube shaped spindle, (2) dipping said mounted support in a supply of liquid emulsion, (3) removing the coated mounted support from the said supply of liquid emulsion and rotating it for one minute in still air about its long axis with its free end inclined upward from the horizontal the rate of rotating the coated element and the angle of inclination of its axis of rotation being such that the liquid emulsion flows in two directions giving a uniform coating, and (4) drying the uniform emulsion coating by passing slow moving air over the rotating element until the emulsion coating stops flowing.

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