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# AQUEOUS METAL IODIDE SOLUTION FOR USE AS AN X-RAY CONTRAST AGENT

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The present invention relates to a method of and masking agents for non-destructive tests, and more particularly to a method of and masking agents for non-destructive tests using penetrating radiation or radioactive rays such as X-rays, gamma rays, and masking agents for such non-destructive tests.

In recent years, with development of industries, non-destructive tests by radioactive rays have come to play an important role in testing metallic materials for detection of interior defects or flaws of castings and and inspection of defects in welded parts. When, however, such methods are applied to material of complicated configuration having various unevennesses or bends, fogs of film occur due to the scattered radiation, and as a result, the image obtained frequently becomes unclear and vague, particularly at the edges of the material tested. In this case, however, the image may be improved by taking a photograph under controlled test conditions, for instance, at a low electric current by using a high voltage X-ray tube and low sensitive film. However, this method is accompanied by the disadvantage that the resolving power is lowered. Thus, in the testing of various shaped materials having parts of different thicknesses, attempts have been proposed to take a photograph by applying lead plate to the thinner parts or using a mold made of low fusible alloy containing heavy metal such as bismuth and shaped in conformity with the specimen. It is, however, impossible to apply such a method to material of complicated configuration as it is difficult to carry out. It has also been proposed to irradiate the material to be tested with radioactive rays, while immersed in a liquid-mask composed of an aqueous solution of lead acetate and lead nitrate, or while coated with a paste of barium sulfate. Such methods are generally insufficient to mask the radiation or radioactive rays. At present, accordingly, only unsatisfactory and unclear images are obtainable with non-destructive tests using radioactive rays, except with specimens of simple shape.

An object of the present invention is to provide a sharp image excellent in contrast of the edge portions of the material tested, especially when testing materials of complicated configuration, in a method of non-destructive testing using penetrating radioactive rays.

Another object of the present invention in to provide a new liquid-mask for radioactive rays suitable for use in a method of non-destructive testing, using the penetrating radiation.

These and other objects of this invention are accomplished by using an aqueous masking solution of an iodide or iodides selected from the compounds of the following group, in carrying out the non-destructive tests, using penetrating radiation:

(a) Zinc iodide.
(b) Cadmium iodide.
(c) Iodides of zinc and alkali metals.
(d) Iodides of zinc and alkaline earth metals.
(e) Iodides of cadmium and alkali metals.
(f) Iodides of cadmium and alkaline earth metals.

In the hitherto known liquid-mask containing lead acetate and lead nitrate, the solubility of both salts in water is low and generally in the order of 50 grams/100 grams $H_2O$ at 15° C. Consequently, in the case where a solution of high concentration is needed as in the test of iron material, the solubility has to be increased by raising the temperature. Therefore, obstacles due to acidity of solution as well as obstacles accompanied by acetic acid vapor and nitric acid vapor have been inevitable. However, in the aforesaid iodide or iodides according to the present invention, the solubility in water amounts to approximately 100 to 200 grams/100 grams $H_2O$ or thereabove even at room temperatures. Moreover, in the case of lead acetate and lead nitrate as set forth above, the acetic acid radical or nitric acid radical which is over one-thirds by weight of lead acetate or lead nitrate does not display any masking action on radioactive rays, whereas in the iodide or iodides of the present invention, there is provided an advantage that the iodine occupying the major part of the above-mentioned iodide demonstrates not only a masking power substantially comparable to that of copper, but the remaining metallic atoms also have effective masking action on radioactive rays. The iodide and iodides are dissolved in water as such or in the form of complex ions. However, the form of their dissolution has no relation with the characteristics of the present invention. Inasmuch as the iodide is dissolved uniformly in solution, alcohol, ether and ketone may be added to the solution.

Materials capable of being tested according to the present invention are metallic material such as iron, aluminum, copper, brass and the like as well as ceramic material of high density such as fused refractory material and the like. The kind and concentration of the solutions are selected, depending on the kind of material to be tested as well as conditions of the test. Satisfactory results are obtained when a solution having masking action corresponding to above 30%, preferably about 50% of the masking action for radioactive rays of the material to be tested is used. For testing of iron materials, for instance, a 50 to 80% by weight aqueous iodide solution is used, and for testing of aluminum material and fused refractory material, for instance, an approximately 20% by weight aqueous iodide solution is used.

The aqueous solution containing the iodide or iodides according to the present invention may liberate iodine in the course of its manufacture and during its storage. Inasmuch as the iodine thus liberated does not evaporate in air and is dissolved in the solution, the masking action for radioactive rays is not affected thereby. However, the strong coloring or turbidity produced in the solution is not only unfavorable, but also the possibility of the test material being corroded will be increased. Therefore, it is preferable to add a reducing agent and alkali to the solution.

For example, hydroxylamine and thiosulfate are specified as a suitable reducing agent. The amount of reducing agent to be added is not constant, but varies in accordance with the amount of free iodine contained as impurity in the raw material as well as with an amount of reducing impurities such as ferrous salt and the like. When an iodide containing a large amount of liberated iodine is used, powder, bar or foil of metallic zinc is added thereto at the time the liquid mask is produced, or the amount of the aforesaid reducing agent is increased. When the content of reducing impurities is high, the amount of reducing agent to be added is decreased. The amount of reducing agent finally existent in the solution preferably is such that the Index of Reductant as hereinafter defined is 5 to 100. A large excess of reducing agent is liable to cause precipitation. Furthermore, when thiosulfate is used alone in a large amount, precipitation occurs sometimes, and consequently, thiosulfate is used preferably in combination with hydroxylamine.

## DEFINITION OF INDEX OF REDUCTANT

The condition in which the solution contains a reducing agent in an amount to reduce 1 milligram equivalent of iodine in 5 cc. of the solution is referred to as index of reductant 50.

As the iodide solution in the present invention is extremely high in concentration, it is practically impossible to measure its pH, and the amount of alkali to be added to the solution has to be so determined that Index of Alkalinity as defined below may range from 2 to 25.

## DEFINITION OF INDEX OF ALKALINITY

5 cc. of an aqueous iodide solution are mixed with 100 cc. of water and the mixture titrated with a 1/10 N aqueous HCl solution. The number of cc. of the 1/10 N aqueous HCl solution consumed until the indicator, methyl red turns red, is defined as the index of alkalinity.

When the index of alkalinity is too high, precipitation of zinc or cadmium hydroxide will occur. Conversely, when the index of alkalinity is below the necessary amount, the solution will be subject to oxidation due to air, and also the material to be tested is liable to be corroded. Oxides or hydroxides of alkali metals, such as caustic potash or caustic soda, or their aqueous solutions are used as alkali.

The iodide solution prepared as above will not show any changes in its appearance even when exposed to the atmosphere for at least 20 days. However, if such iodide solution is left to stand for an extended period of time, the index of reductant and index of alkalinity will decrease, and thus, iodide deposition takes place or finally precipitation occurs. However, such a solution may be used after the precipitate is removed. It is appropriate to reuse the solution after adding the reducing agent and alkali thereto. When iodides of alkaline earth metals are used in combination with zinc or cadmium iodides, there is the tendency to precipitate carbonate by absorbing carbonic acid gas from atmospheric air. The formation of carbonate has been ascertained not to impart any appreciable effect to the measured result in the non-destructive test. Generally, however, it is rather preferable not to use alkaline earth metals, in order to avoid such occurrence of the precipitation.

Materials to be tested, such as iron, steel, copper, tin or their alloys will almost not be corroded, even after at least 20 days immersion in the aqueous iodide solutions according to the invention. Only some discoloration occurs at a gas-liquid contact portion after an extended period of time. In some cases, it is effective to apply a grease or the like to material to protect it from corrosion. Particularly when the material to be tested is subject to corrosion, it is appropriate to provide a corrosion-resisting coating around the said material. For instance, the material is immersed in a butyl acetate solution of polyvinyl-butyral and withdrawn after a suitable period of time, to form a corrosion-resisting synthetic resin coating on its surface. This coating may be readily removed after the test. Furthermore, in order to improve the foaming characteristics at the time when material to be tested is immersed in a solution, a defoaming agent, such as surface active agent or the like may be added.

In practicing the method of non-destructive testing using the liquid-mask according to the present invention, the aforementioned aqueous iodide solution is put in a suitable receptacle or vessel permeable to the penetrating radiation or the radioactive rays, and the whole or a part of the material to be tested is immersed in the solution contained in said receptacle. Then, the test may be conducted by irradiating the test material in the solution with the radioactive rays by a known method. In the case where the material to be tested cannot be immersed in a solution, the solution is sealed in a deformable bag-like receptacle made of a sheet of polyethylene, vulcanized rubber and the like, and then the receptacle is applied against the material to be tested and irradiated with radioactive rays. As means for detecting the radioactive rays or penetrating radiation, any of the known means, such as, photography using a light-sensitive film, or fluoroscopic observation is suitably adapted. Furthermore, when the deformable bag-like receptacle is to be filled with a solution, it is preferable to add a soluble starch, gelatine and agar-agar thereto, in order to lower the fluidity of the solution. Any suitable permeable radiation or radioactive rays which are generally usable for such a purpose, such as, X-rays and gamma rays can be used as a source of radiation for the non-destructive tests according to the invention.



Thus, according to the present invention, scattered radioactive rays having a deleterious effect upon the film are masked and the whole surroundings including the materials to be tested can be also subjected to penetrating radiation or radioactive rays under substantially uniform conditions. Therefore, regardless of the configurations and properties of the material to be tested, a sharp image excellent in contrast of the edge portions can be obtained. Moreover, even when the photography is effected under conditions generally liable to cause fog, a clear distinct image may be readily and surely obtained.

This invention is further described in the following examples which are illustrative and not limitative thereof.

### *Example 1*

450 grams of zinc iodide and 350 grams of potassium iodide were dissolved in 200 grams of water, and then 10 grams of hydroxylamine hydrochloride were added to the solution. Thereafter, a caustic potash solution was gradually dropped into the mixture while the index of alkalinity was detected. The light yellowish solution thus obtained had a specific gravity of 2.52, an index of alkalinity of 20, and an index of reductant of 45. At various X-ray tube voltages (kv.p.=kilovoltage peak), the iron equivalent of the aqueous solution of under-mentioned respective thicknesses (mm.) [which means thickness (mm.) of iron showing the same masking power for radioactive rays as that of the solution] was measured, the results being as follows:

| | Tube voltage | | |
|---|---|---|---|
| | 250 | 200 | 150 |
| Thickness of liquid: | | | |
| 10 | 9 | 9 | 10 |
| 20 | 14 | 16 | 18 |
| 30 | 20 | 23 | 25 |
| 40 | 26 | 29 | ---- |
| 50 | 31 | 35 | ---- |

In the next place, an iron material to be tested of 20 mm. in thickness and having a sectional form of a rectangular piece 15 x 50 mm. secured at a side of its bottom to another rectangular piece 5 x 40 mm. in L-shape was immersed in this solution, and a photograph was taken by exposing to X-rays at 4 ma. for 1.5 minutes in the vertical direction to said section by using X-ray tube of 250 kvp. Then, an image of clear configuration and excellent in contrast was obtained.

When the same test material was photographed in air without immersing into said solution, the image in the narrower portion was entirely unclear because of fog. Even when various different X-ray tubes were used or conditions of exposure were changed, no clear image could be obtained.

### *Example 2*

1900 grams of zinc iodide were dissolved in 630 grams of water, and 1 gram of hydroxylamine hydrochloride and 0.2 gram of sodium thiosulfate admixed with the resulting solution. Then, the index of alkalinity was adjusted to 20 by gradually dropping in a 5% caustic potash solution. The thus-obtained colorless semi-transparent solution of specific gravity 2.4 had an index of

reductant of 11. The iron equivalents of the solution measured in the same manner as in Example 1 were as follows:

| | Tube voltage | | |
|---|---|---|---|
| | 250 | 200 | 150 |
| Thickness of liquid: | | | |
| 10 | | 9 | 10 |
| 20 | 15 | 17 | 19 |
| 30 | 21 | 23 | 28 |
| 40 | 27 | 30 | 36 |
| 50 | 32 | 35 | 44 |

When this solution was used and a specimen similar to that used in Example 1 was photographed under the same condition, a clear image was obtained.

*Example 3*

1400 grams of cadmium iodide and 1700 grams of calcium iodide hydrate were dissolved in 900 grams of water, and a solution containing 35% cadmium iodide and 35% calcium iodide was obtained. When 2 grams of hydroxylamine hydrochloride, 2 grams of sodium thiosulfate and 20 grams of potassium hydroxide were added and dissolved in the solution, the solution obtained showed specific gravity of 2.13, an index of reductant of 8.85 and an index of alkalinity of 3.36. The iron equivalents measured similarly as in Example 1 were as follows:

| | Tube voltage | | |
|---|---|---|---|
| | 250 | 200 | 150 |
| Thickness of liquid: | | | |
| 10 | 7 | 8 | 9 |
| 20 | 13 | 14 | 17 |
| 30 | 18 | 20 | 24 |
| 40 | 24 | 26 | ---------- |
| 50 | 29 | 33 | ---------- |

When this solution was used and a photograph was taken of a specimen similar to that used in Example 1, under similar conditions, a clear image was obtained.

*Example 4*

180 grams of soluble starch (Japanese trademark: Miraclin) were added to 500 cc. of a 75% by weight zinc iodide solution obtained as in Example 1 (sp. gravity, 2.4; index of alkalinity, 20 and index of reductant, 11) and dissolved therein while heating. The thus-obtained solution having fluidity but of remarkably high viscosity was filled in a polyethylene bag of 0.1 mm. thickness, de-aerated under reduced pressure and immediately thereafter its mouth was sealed. This bag was caused to adhere firmly to hollow portions and surroundings of the material to be tested, so as to become uniform in thickness. Then, the photograph was taken by irradiating the material to be tested with radioactive rays, and a clear image was obtained.

What is claimed is:

1. In carrying out a non-destructive test by irradiating a material to be tested with penetrating radiation; the step of masking the material to be tested by an aqueous metal iodide solution having masking power for the penetrating radiation approximately similar to that of said material to be tested during the irradiation, the aqueous metal iodide solution being selected from the group consisting of aqueous solutions of:
(a) zinc iodide,
(b) cadmium iodide,
(c) iodides of zinc and alkali metal,
(d) iodides of zinc and alkaline earth metal,
(e) iodides of cadmium and alkali metal, and
(f) iodides of cadmium and alkaline earth metal.



2. In carrying out a non-destructive test by irradiating a material to be tested with penetrating radiation; the steps of immersing the material to be tested in an aqueous metal iodide solution having masking power for the penetrating radiation approximately similar to that of said material to be tested during the irradiation, the aqueous metal iodide solution being selected from the group consisting of aqueous solutions of:
(a) zinc iodide,
(b) cadmium iodide,
(c) iodides of zinc and alkali metal,
(d) iodides of zinc and alkaline earth metal,
(e) iodides of cadmium and alkali metal, and
(f) iodides of cadmium and alkaline earth metal.

3. In carrying out a non-destructive test by irradiating a material to be tested with penetrating radiation; the steps of masking the material to be tested by a deformable bag-like receptacle containing an aqueous metal iodide solution having masking power for the penetrating radiation approximately similar to that of the material to be tested, the metal iodide being selected from the group consisting of aqueous solutions of:
(a) zinc iodide,
(b) cadmium iodide,
(c) iodides of zinc and alkali metal,
(d) iodides of zinc and alkaline earth metal,
(e) iodides of cadmium and alkali metal, and
(f) iodides of cadmium and alkaline earth metal.

4. In carrying out a non-destructive test by irradiating a material to be tested with penetrating radiation; the step of masking the material to be tested by an aqueous zinc iodide solution having masking power for the penetrating radiation approximately similar to that of the said material during the irradiation.

5. In carrying out a non-destructive test by irradiating a material to be tested with penetrating radiation; the step of masking the material to be tested by an aqueous solution of zinc iodide and alkali metal iodide having masking power for the penetrating radiation similar to that of the said material during the irradiation.

6. A method of a non-destructive test as set forth in claim 1, wherein the aqueous iodide solution contains a reducing agent and alkali.

7. A liquid-mask for a non-destructive test, comprising an aqueous metal iodide solution selected from the group consisting of aqueous solutions of:
(a) zinc iodide,
(b) cadmium iodide,
(c) iodides of zinc and alkali metal,
(d) iodides of zinc and alkaline earth metal,
(e) iodides of cadmium and alkali metal, and
(f) iodides of cadmium and alkaline earth metal, said aqueous metal iodide solution also comprising an alkali and a reducing agent dissolved therein.

8. A liquid-mask for a non-destructive test, comprising an aqueous metal iodide solution selected from the group consisting of aqueous solutions of:
(a) zinc iodide,
(b) cadmium iodide,
(c) iodides of zinc and alkali metal,
(d) iodides of zinc and alkaline earth metal,
(e) iodides of cadmium and alkali metal, and
(f) iodides of cadmium and alkaline earth metal, said aqueous metal iodide solution also comprising thiosulfate, hydroxylamine and alkali dissolved therein.

9. A liquid-mask as set forth in claim 7 having the index of reductant of 5 to 100, as defined in the specification.

10. A liquid-mask for a non-destructive test, as set forth in claim 7 having the index of alkalinity of 2 to 25, as defined in the specification.

11. A liquid mask for a non-destructive test comprising an aqueous solution of zinc iodide, thiosulfate, hydroxylamine and alkali.

12. A liquid mask for a non-destructive test comprising an aqueous solution of zinc iodide, alkali metal iodide, thiosulfate, hydroxylamine and alkali.

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