Feb. 24, 1959 F. NESH 2,875,341

PREPARATION OF REPLICA SPECIMENS FOR EXAMINATION UNDER ELECTRON MICROSCOPE

Filed Sept. 25, 1957 2 Sheets-Sheet 1

Fig. 1.

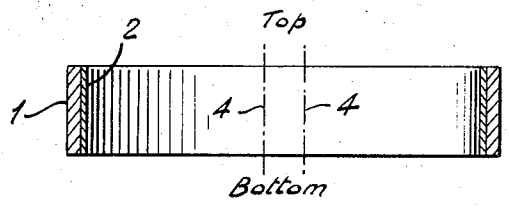


Fig. 2.

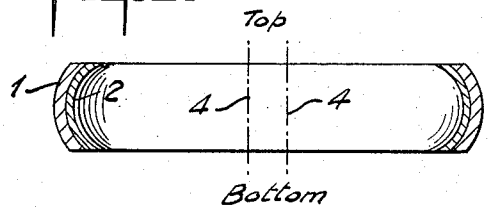


Fig. 3.

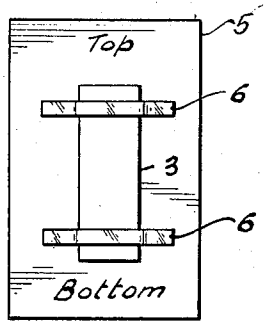


Fig. 4.

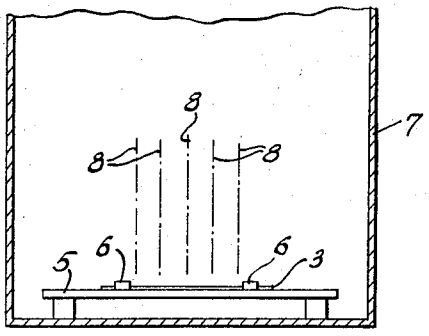
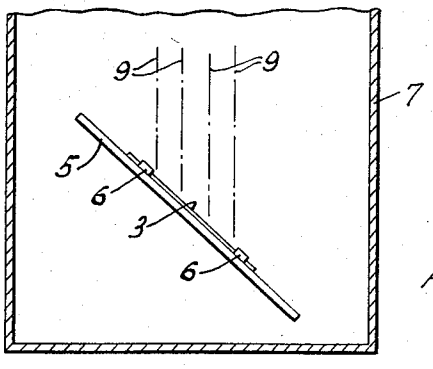


Fig. 5.



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PREPARATION OF REPLICA SPECIMENS FOR EXAMINATION UNDER ELECTRON MICROSCOPE

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Fig. 6.

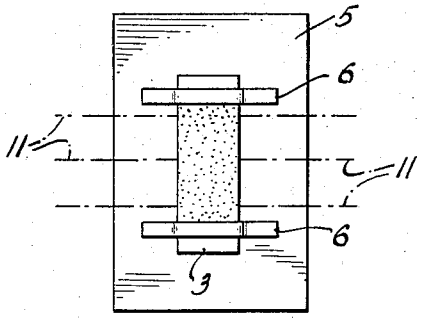


Fig. 7.

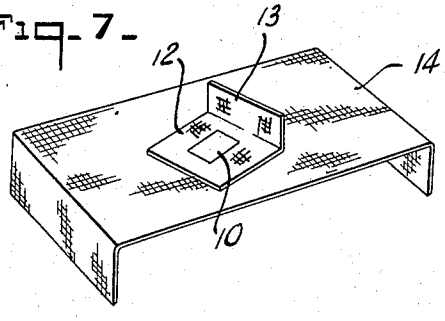


Fig. 8.

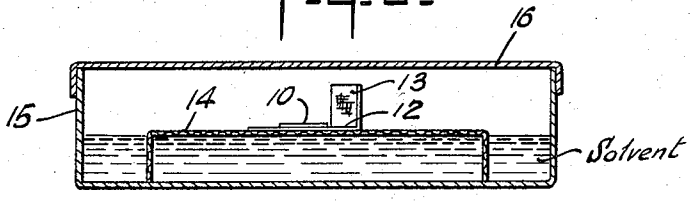
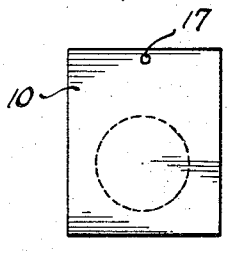


Fig. 9.



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PREPARATION OF REPLICA SPECIMENS FOR EXAMINATION UNDER ELECTRON MICROSCOPE

Florence Nesh, Brooklyn, N. Y.

Application September 25, 1957, Serial No. 686,267

12 Claims. (Cl. 250—49.5)

(Granted under Title 35, U. S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment off any royalties thereon or therefor.

This invention relates to the preparation of replica examples of a surface for examination in an electron microscope, which may be used to give total electron microscope coverage of a surface in small increments. It is impractical to examine a surface of substantial size in an electron microscope, and therefore it has usually been necessary to prepare a replica sample of selected portions of the surface and examine the replica surface.

An object of the invention is to provide an improved method for preparing a replica example of a surface to be examined, and from such sample providing a replica specimen that can be mounted for examination in an electron microscope, with which such specimen will have maximum possible, accurate representation of said surface to be examined, which makes unnecessary the tedious process of fishing out cut pieces of replica from a solvent bath, with which the replicating media do not chemically or physically change the surface under examination, which may be used to replicate any metallic surface before or after etching, which may be successfully used to examine the surface of an object of any material, and which will be relatively simple, rapid, practical, easily performed with a minimum of apparatus, and of low cost.

Another object is to provide an improved method for this purpose, which will eliminate false indications and artifacts introduced into the replica by strain during its removal from the surface, which results in practically 100% efficiency in replication and saves operating time, and which makes unnecessary the forceful separation of the plastic replica from the surface to be examined.

Other objects and advantages will appear from the following description of a practical application of the method, and the novel features will be particularly pointed out hereinafter in connection with the appended claims.

In the accompanying drawings:

Fig. 1 is a sectional elevation of one type of ring surface, with a plastic replicating coating applied thereto, and showing where a sample of the coating is taken;

Fig. 2 is a sectional elevation of another type of ring surface, such as a ball bearing race, with plastic replicating coating applied thereto, and showing where a sample of the coating is taken;

Fig. 3 is a plan of a microscope slide with the sample of the coating mounted thereon, illustrating an intermediate step in the method;

Fig. 4 is a side elevation of the same, and illustrating schematically the manner in which a coating of a replication medium may be applied by vacuum deposit;

Fig. 5 is a similar schematic elevation illustrating how a coating of a shadowing material may be applied to the sample by vacuum deposit;

Fig. 6 is a plan of the slide with the sample mounted thereon, and after application to the sample of the replication medium and the shadowing material, and illustrating the manner in which specimens are taken from the sample;

Fig. 7 is a perspective illustrating how the specimens are mounted for removal therefrom of the plastic coating material;

Fig. 8 is a diagram illustrating how the mounted specimen of Fig. 7 is placed in a closed chamber containing a solvent for the plastic coating material; and

Fig. 9 is a plan, on a larger scale, of the specimen after the plastic coating material has been removed, and showing how a portion of this specimen is removed for mounting for use in an electro microscope.

The method, certain steps of which are illustrated in the drawings, makes use of the fact that a film of plastic replicating material when applied to the inner surface of a ring, shrinks upon drying, and so separates itself from the surface of the ring without any special action or artificial means, thereby eliminating false indications and artifacts introduced into replicas by strain during removal of such replicas from the surface to be examined. It also eliminates the tedious process of recovering floating cut pieces of scored replica from a solvent bath. It is necessary that the surface under study form part of the inner surface of a ring, in order that the replica film applied thereto, separate itself, by shrinking while drying, from such inner surface. If the surface to be studied already is part of a cylindrical system, or if the specimen can be cut so as to provide a ring with an inner surface, the method can be used therewith directly. If the normally applied replicating plastic coating does not form a ring, a convenient attachment to extend the surface so that it forms part of a cylinder or ring can be made. For purposes of illustration, the method will be described as employed in examining the inner surface of a ball bearing race.

In the practice of the method, the inner surface of the race should be first cleaned, as with benzol. To the cleaned surface one next applies a coating of a relatively thin solution of a replicating plastic material, such as a 1% solution of polystyrene in benzol. This coating is allowed to dry and then a second layer applied of this 1% solution and allowed to dry. Then one applies over the previous coatings a 3% solution of the polystyrene in benzol and allows that coating to dry. Next a coating is applied over the previous coatings of a 6% solution of polystyrene in benzol. The race **1** with all of these coatings **2** is then allowed to stand at least about 24 hours, and possibly as long as 72 hours, until the polystyrene begins to shrink and break away from the inner surface of the race. The circular strip **2** of polystyrene is then cut, where it has become separated from the race, across the strip into strips **3** about 2 mm. wide, noting the exact area from which each piece was cut. The dot and dash lines **4** in Figs. 1 and 2 illustrate how the strip is cut.

Each of these 2 mm. strips **3** is then mounted on a rigid plate **5** such as a glass microscope slide. For example strips **6** of Scotch or pressure sensitive tape may be used to confine the ends of the 2 mm. strips to the plate **5** adjacent the ends of strips **3**. Notation is made on this plate **5** as to which are the top and bottom edges of the mounted strip **3**, as shown in Fig. 3.

The plate **5** with a strip **3** mounted on a face thereof is then placed in a housing **7** (Fig. 4) of a vacuum depositor, well known in the art, where the strip is coated with a replication medium such as colloidal silica. The direction of deposit of such medium is schematically illustrated by the dot and dash lines **8** in Fig. 4. The plate **5** with the silica coated strip **3** thereon, is

then disposed at an oblique angle in a housing 7 and the strip 3 is then shadowed by vacuum deposit on the strip of a suitable shadowing material such as germanium. The direction of deposit of the germanium is illustrated in Fig. 5 by the dot and dash lines 9.

The strip 3, as thus coated with silica and shadowed with germanium, is removed from plate or slide 5 and cut into small specimens 10 (Figs. 7 and 9) of about 2 mm. square such as by cutting the strip 3 along the dot and dash lines 11 in Fig. 6 and noting the top and bottom edges thereof. One of these specimens 10 is then placed on a small piece 12 of fine wire mesh of electrolytic copper having an upstanding flange 13 by which one may lift the piece 12 with the small specimen thereon. This piece 12 with specimen 10 thereon is then placed on a wire bridge 14 in a closed chamber, such as on the bridge 14 in a small petri disk 15 containing a solvent for the polystyrene or other plastic material. For the polystyrene, benzol is advantageously used as the solvent. The level of the benzol or solvent is just slightly below the piece 12, and preferably the solvent just barely touches the bottom of the bridge. The petri dish is covered by cover 16 to avoid contamination of the replica or specimen 10 and to retard loss or escape of vapors of the solvent. The bridge with the specimen 10 is left in the closed petri dish for about 24 hours, during which time the vapors given off by the solvent in the dish will slowly dissolve much of the polystyrene or other plastic material. The solvent is then changed to 85% ethyl bromide and 15% benzol, and the specimen left subject to the vapors from this new mixture of solvents in the closed chamber for about 2 or 3 days until the specimen is free of all plastic or polystyrene. During this time any solvent vapors lost should be replaced by further solvent.

The specimen so freed of the polystyrene or other plastic is removed from the chamber and air dried for about 24 hours. A pin hole 17 (Fig. 9) is then punched in an edge of the specimen 10 to indicate direction so that when examined under the electron microscope, the direction may be known. The specimen is then mounted for examination under the microscope. While 2 mm. squares were found to be adequate for a detailed study of the surface of the race, one may use other sizes of the squares, such as 1 mm. squares, for example.

This method permits of a systematic study of the entire inner surface of the bearing race, and it may be utilized to replicate any metallic surface before or after etching, and if necessary an attachment may be employed to create the effect of a ring with the surface to be examined on the inside of the ring. Specific areas of nonmetallic surfaces can be studied by this method, using replicating media that do not chemically or physically change the material of the surface under examination.

While ordinary benzol may be employed, the purer thiophene-free benzol is advantageous. Silica is an excellent and commonly used replication medium for vacuum deposition, and the form of silica employed in working examples was colloidal quartz. Other replication mediums are known, such as carbon for example, and any of them may be used in place of quartz. While the shadowing is preferably done with germanium, other shadowing materials are well known and may be used in place of germanium. A few examples of such other shadowing materials are chromium, gold, or any other metal. The wire mesh 12 may be any very fine mesh metallic wire or other material inert to the solvents used. Any replicating plastic material may be used as the original coating material, and such materials are well known in the art and the solvent used will be one for the particular replicating material selected. Polystyrene is very useful for this purpose, gives excellent results when used on metallic surfaces and is relatively inexpensive, so that its use is advantageous and preferred. The solvent for

the polystyrene is preferably benzol or a mixture of benzol and ethyl bromide because they readily vaporize at room temperatures, but other solvents or mixtures thereof may be used.

It will be understood that various changes in the details, steps and materials, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

I claim:

1. The method of preparing replica examples of a surface for examination in an electron microscope, which comprises arranging the surface to be examined as the inner surface of a ring, layering such inner surface with a solution of a replicating plastic material to form a plastic film on said inner surface, drying the layer of plastic material on said surface until the film shrinks enough to break away, at least in part, from said surface, cutting off a strip from the portion of said film that has broken away from said surface, mounting said strip on a rigid plate, vacuum depositing upon such mounted strip first a coating of a replication medium and then upon such coating a shadowing material, supporting a specimen of said strip carrying replication medium and shadowing material upon the top of a fine mesh screen, in a closed chamber above a solvent for said plastic material until the plastic of said specimen has been removed from the specimen, air drying this plastic-free specimen, and mounting part of such air dried specimen for examination under an electron microscope.

2. The method as set forth in claim 1 wherein said plastic material is polystyrene.

3. The method as set forth in claim 1 wherein said plastic material is polystyrene and the solvent is benzol.

4. The method as set forth in claim 1 wherein said replication medium is colloidal silica.

5. The method as set forth in claim 1 wherein said shadowing material is germanium.

6. The method as set forth in claim 1 wherein said replication medium is colloidal silica and the shadowing material is germanium.

7. The method as set forth in claim 1 wherein said layering includes a plurality of successive applications of relatively weak solutions of the plastic material of successively larger ratios of the plastic material, with drying between such applications.

8. The method of preparing replica examples of a surface for examination in an electron microscope, which comprises arranging the surface to be examined as at least a part of the inner peripherally continuous surface of a closed loop, layering said inner surface with a solution of a plastic film material, drying such inner surface with applied material until the film by itself shrinks away from said inner surface to be examined, removing a sample of such film which has shrunk from said inner surface, and then making a transparent replica of that surface of said film sample which had been in contact with said inner surface for mounting in said microscope.

9. The method as set forth in claim 8, wherein said removed sample of said film is formed with a replication medium and then shadowed with a suitable shadowing agent, after which the film is removed, leaving the shadowed replica for mounting in said microscope.

10. The method as set forth in claim 8 wherein said inner surface is the inner surface of a circular ring.

11. The method as set forth in claim 8 wherein said layering includes a plurality of separate applications of thin solutions of a replicating plastic material, with each application allowed to dry before the next application of such solution.

12. The method of preparing replica examples of a surface for examination in an electron microscope, which comprises arranging the surface to be examined as at least a part of a concave, arcuate surface, layering said arcuate,

concave surface to be examined with a succession of dilute solutions of polystyrene, starting at about a 1% solution and increasing by steps to about a 6% solution, with drying between successive layerings and after the final layering to form a film on said surface, and after the film shrinks from said surface, making a replica of that surface of said film which had been in contact with said surface under examination for mounting in said microscope.

References Cited in the file of this patent

UNITED STATES PATENTS

2,347,965	Ramberg	May 2, 1944
2,618,014	Sawyer	Nov. 18, 1952

OTHER REFERENCES

"Electron Optics and the Electron Microscope" (Zworykin, Morton, Ramberg, Hillier, and Vance), published by Wiley (1945), pages 248–52 relied on.