

April 22, 1947.

R. G. TREUTING

2,419,237

TRANSLATING MATERIAL AND DEVICE AND METHOD OF MAKING THEM

Filed Jan. 18, 1945

2 Sheets-Sheet 1

FIG. 7

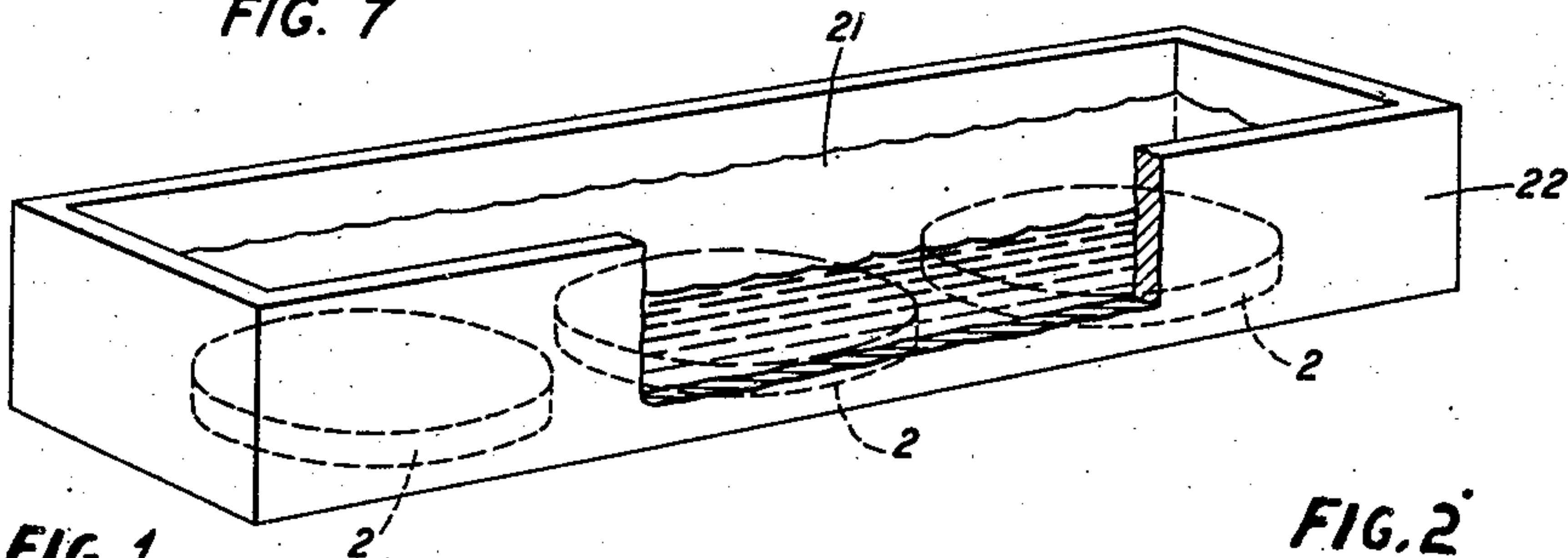


FIG. 1

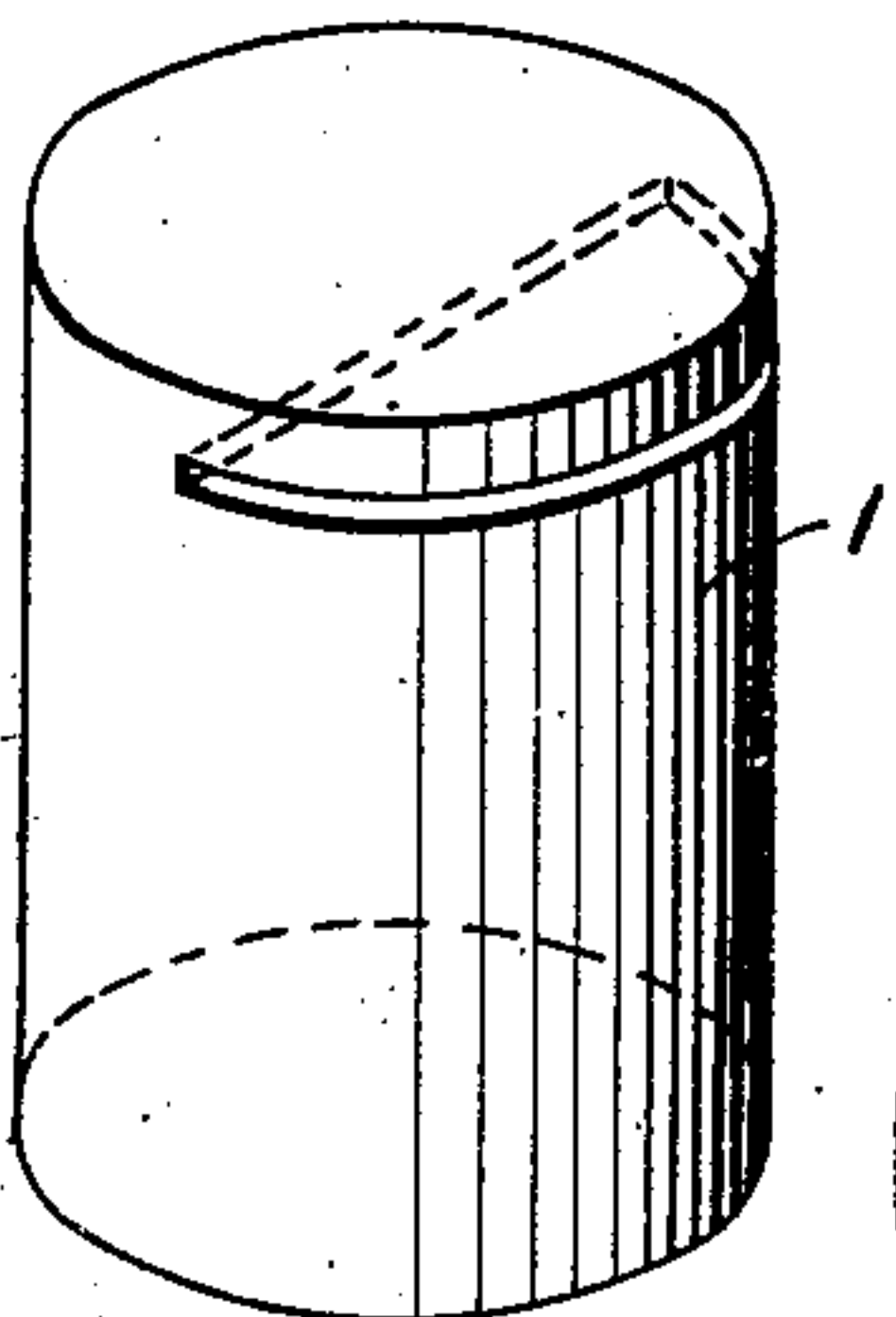


FIG. 8

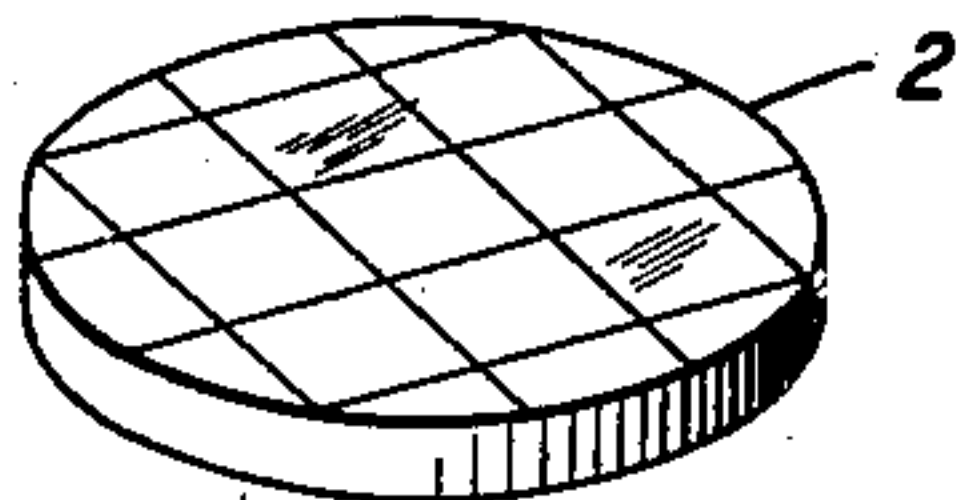


FIG. 2

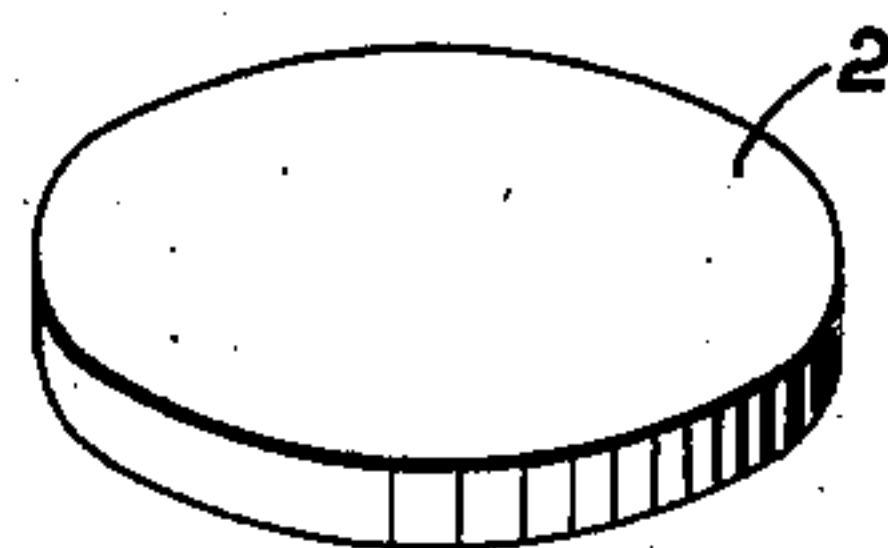


FIG. 9



FIG. 10

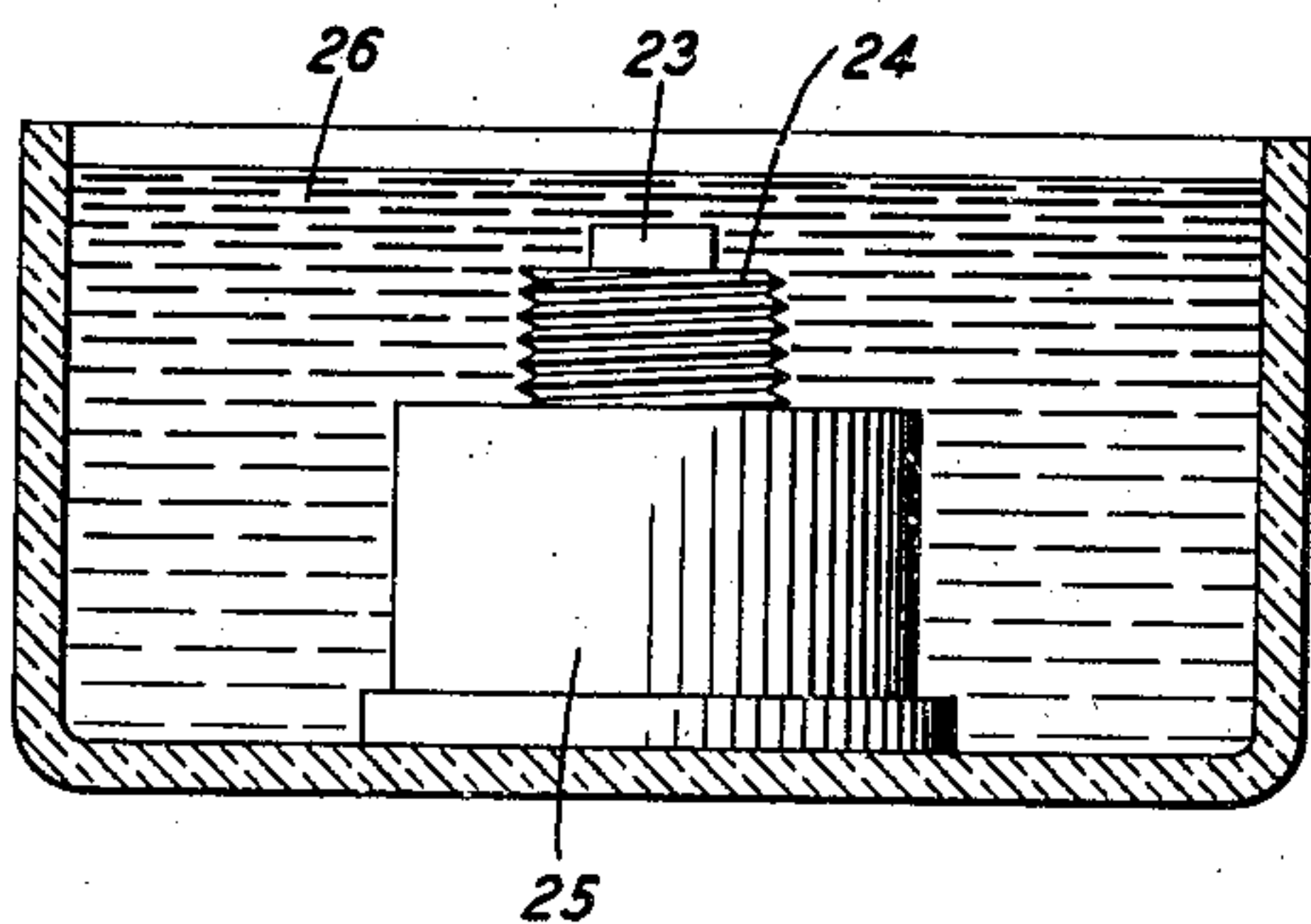
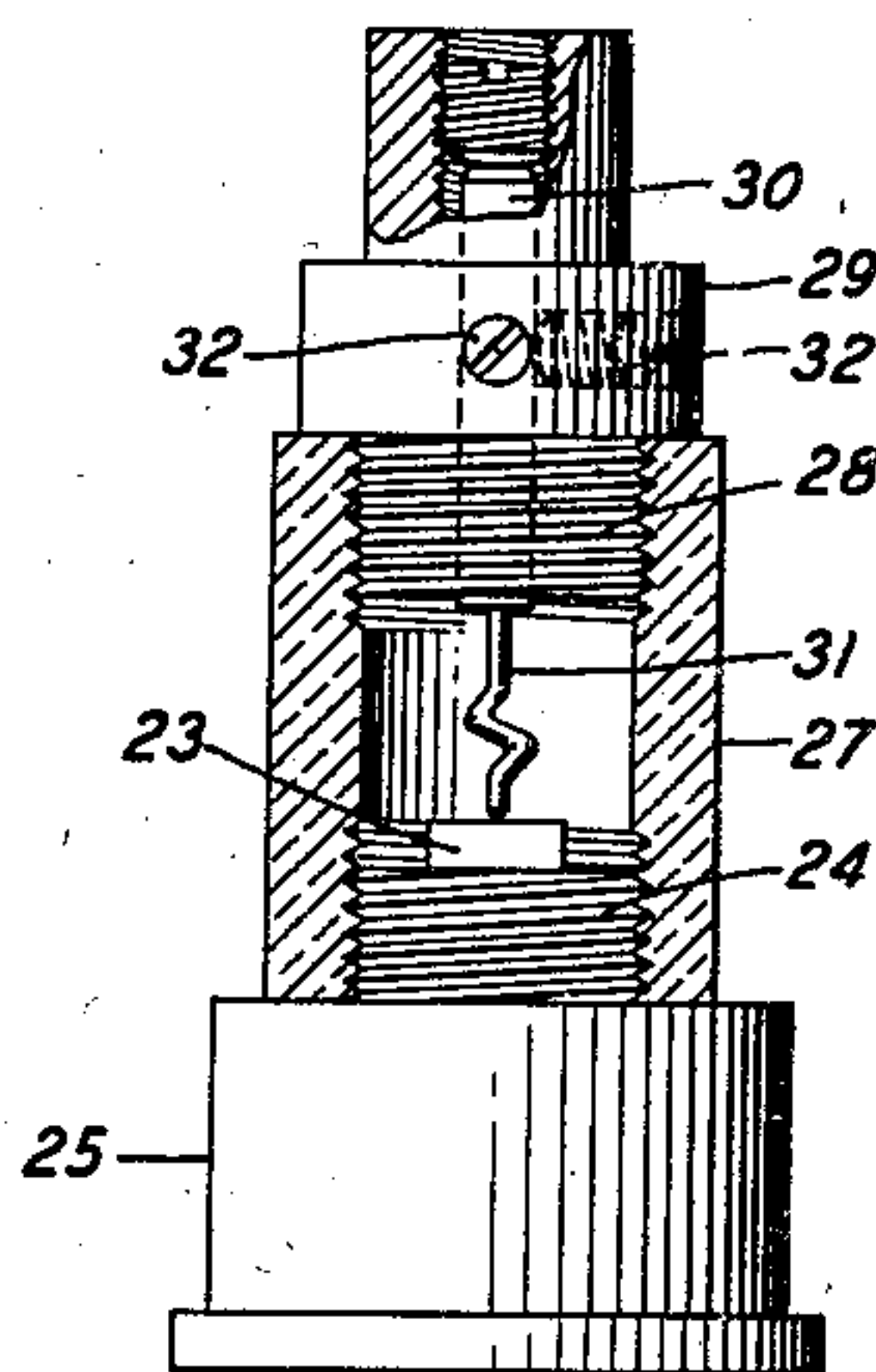


FIG. 11



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2 Sheets-Sheet 2

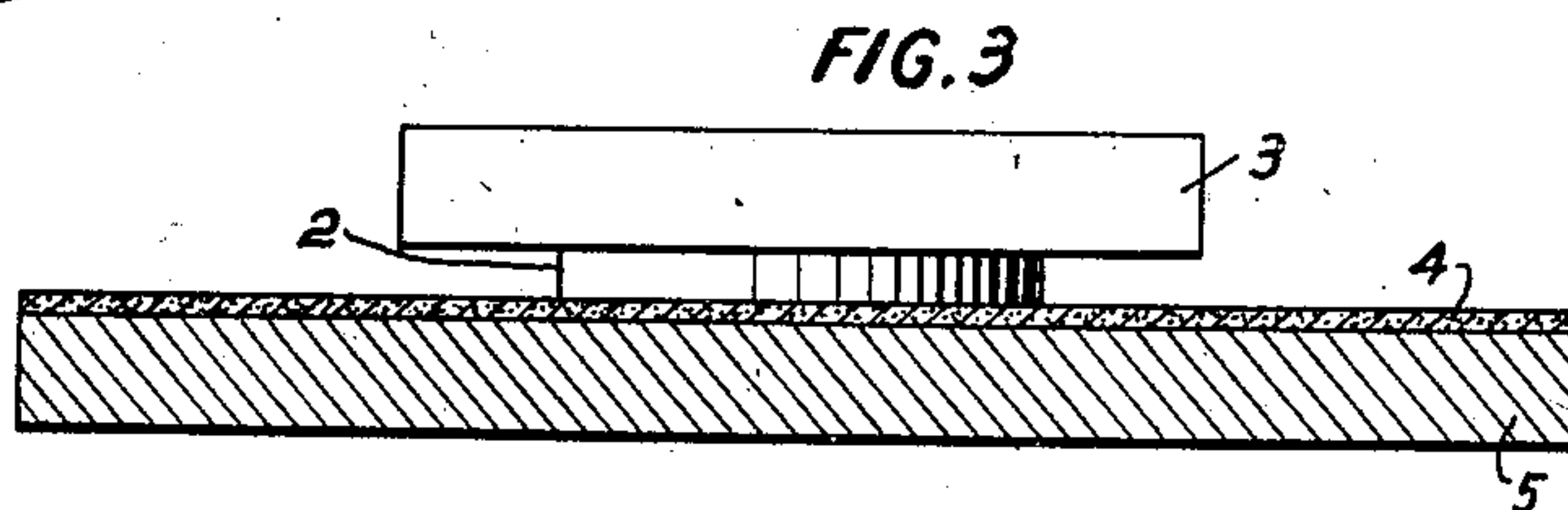
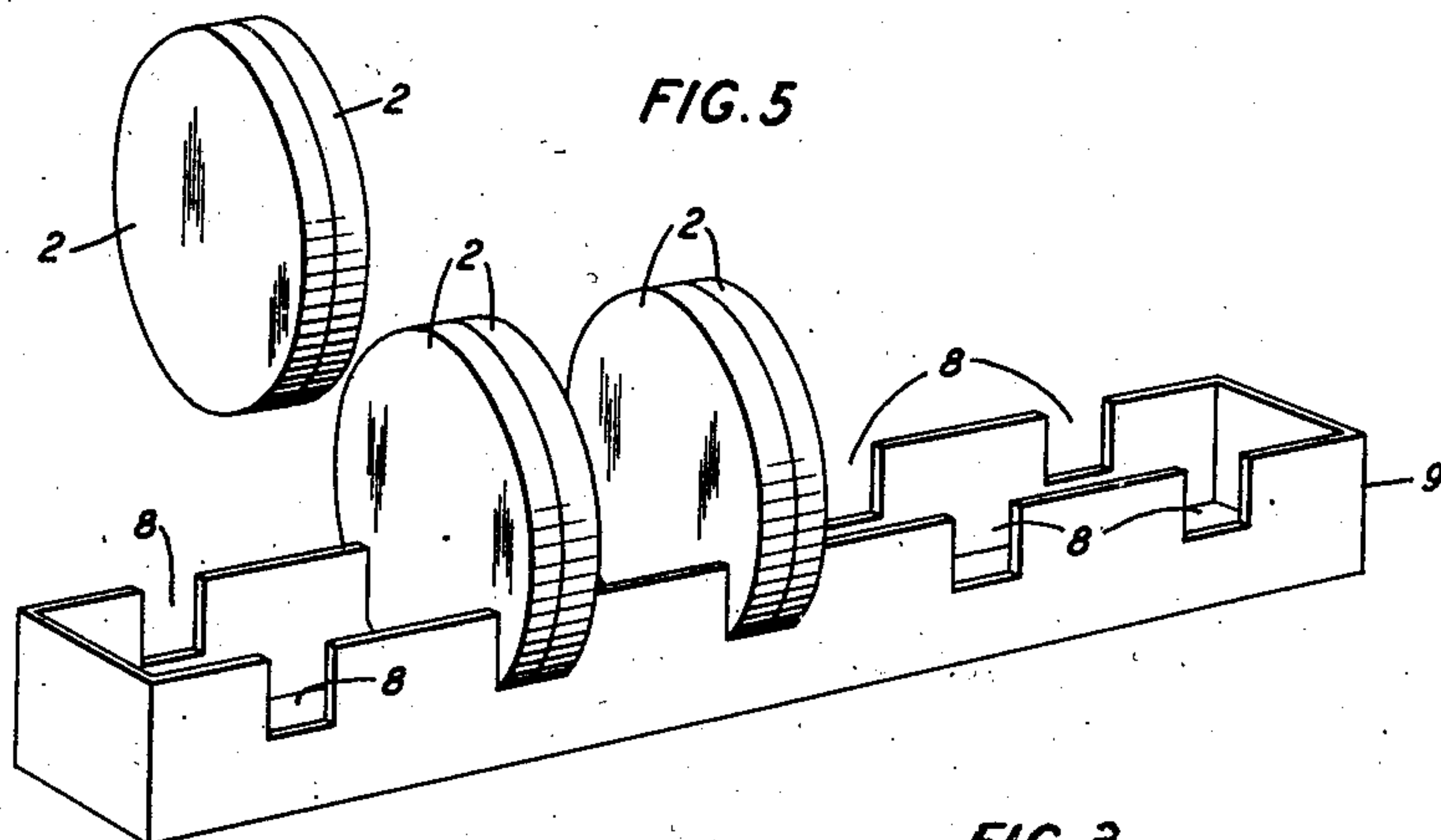


FIG. 6

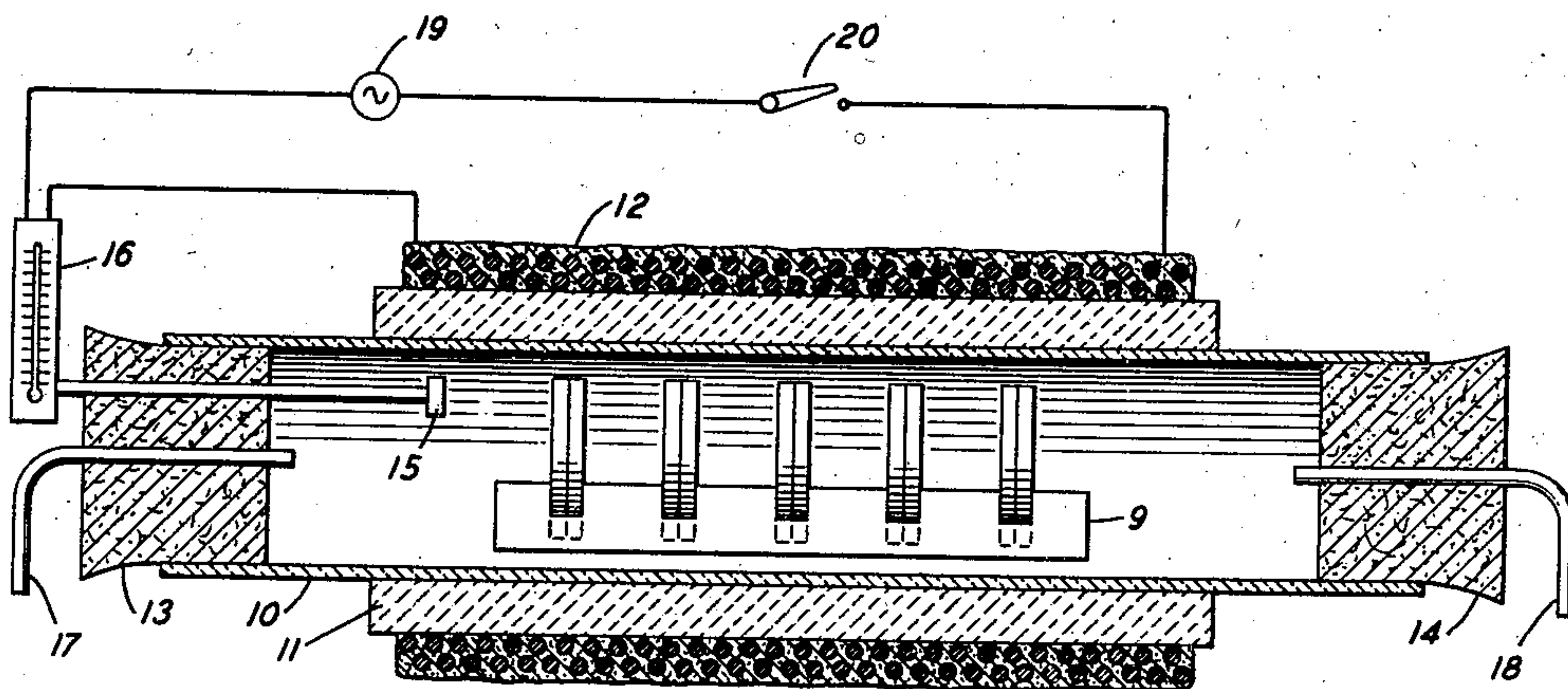
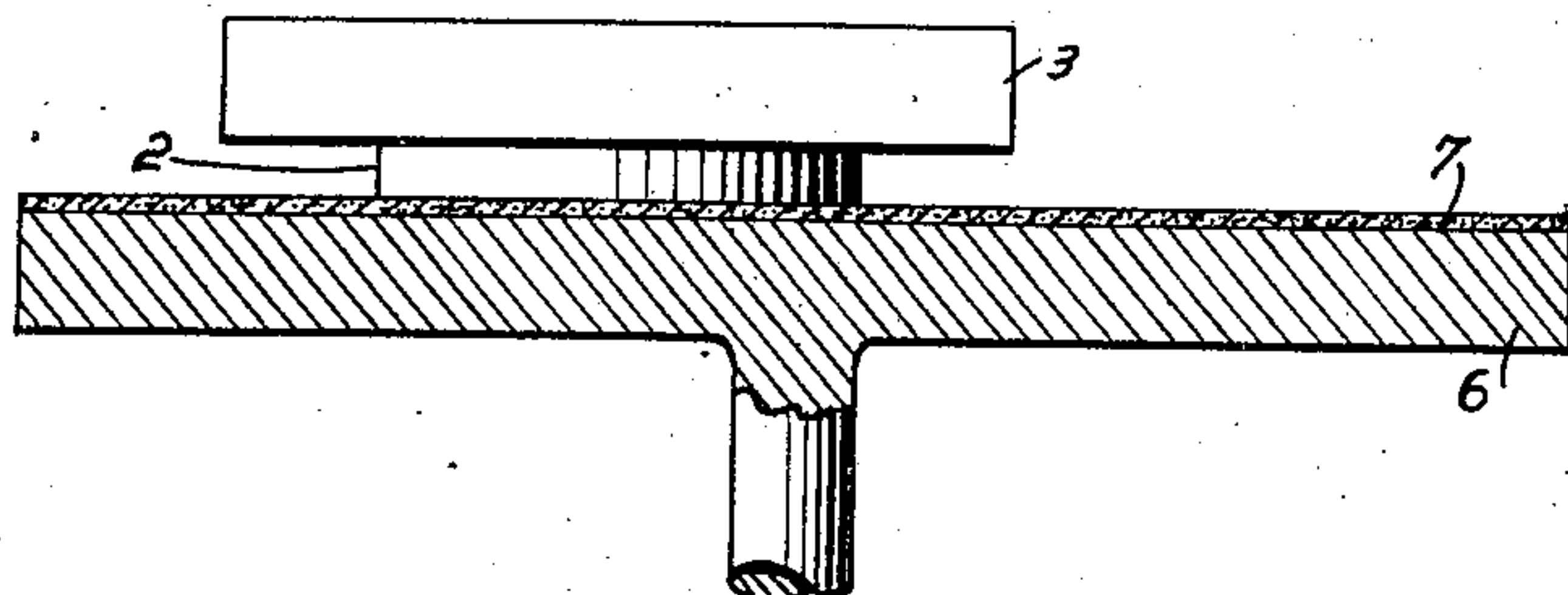


FIG. 4



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2,419,237

TRANSLATING MATERIAL AND DEVICE AND
METHOD OF MAKING THEM

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Application January 18, 1945, Serial No. 573,414

9 Claims. (Cl. 250—31)

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This invention relates to conducting and translating materials and devices and to methods of making them.

The objects of the invention are to improve the electrical properties of conducting and translating materials; to shorten the time required in their preparation; to effect a substantial reduction in the temperatures employed in the heat treatment of these materials; to reduce the deterioration of the heating apparatus; to realize an improvement in the conversion loss and noise factors of these materials when used in translating devices; to facilitate the final adjustment of the assembled devices to obtain the desired characteristics therefor; and to effect other improvements in materials and devices of this nature and in the methods of making them.

It has been the practice heretofore in the preparation of microwave rectifiers of the point-contact type to use a rectifying element of crystalline silicon of very high purity and to subject the crystal element, before assembling it in the rectifier structure, to a heat treatment process. The primary purpose of the heat treatment is to eliminate the impurities near the surface and to form thereby a thin layer of silicon which is found to give the crystal element unusually good translating properties. Since the impurities are to a large extent of a metallic nature, they are converted to oxides by the heat treatment and removed from the surface, leaving the desired silicon layer on the surface of the crystal element. This process is conducted at fairly high temperatures and heretofore has required a matter of hours. One difficulty which has been experienced is the natural tendency of the impurities in the crystal element to migrate or diffuse toward the surface in response to the heating. And this is true particularly when substantial amounts of additional materials, such as boron, are included, for desirable reasons, in the silicon element during its preparation. Accordingly the long application of the heat treatment necessary to oxidize the metallic impurities results in a greater diffusion of impurities from the body of the element up into the surface layer, thus impairing the translating properties being sought. Furthermore, these long heat treatments cause undue deterioration of the heating apparatus used in the process; also they do not permit the most advantageous use of the apparatus nor of the working time of the attendant.

With these considerations in mind applicant has found that he can overcome the objections above noted and can also secure other important

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advantages by replacing the single continuous heat treatment heretofore used with a plurality of successive treatments, each of which is of a much shorter duration. More specifically, and by way of example, the silicon crystal element may be subjected to two separate relatively short heat runs, each at 1000° C., instead of the single continuous run to two or more times the duration previously required at that temperature or perhaps at the increased temperature of 1050° C. By reducing the period of the heat run the amount of oxidation is greatly increased in comparison to the amount of diffusion. At the end of the first short run the crust or coating of oxide is removed by an etchant preparatory to the next run. This removal of the coating formed during the first run fully exposes the surface to the atmosphere within the heat chamber during the second short run and thus maintains the favorable relation between the rate of oxidation and the rate of diffusion. As many of these separate short runs may be made as is found desirable.

As alluded to above, one of the chief advantages of applicant's process is the attainment of a translating element which is superior in its rectification performance. Another and a related advantage has to do with the assembly of the translating element in a rectifier structure and the adjustment of the contact forming parts. One of the last steps in the assembly process is to advance the fine point of the spring contact wire into engagement with the prepared surface of the silicon element until the requisite degree of pressure is obtained. The final step is to tap the rectifier structure with gentle blows until the contact point formed by the wire on the silicon surface assumes the desired electrical characteristics. In the past this tapping step has required considerable skill as well as time on the part of the operator, but the material prepared in accordance with applicant's process responds much more readily to the tapping operation and requires less time and skill.

The foregoing and other features and advantages of the invention will be described more fully in the following detailed specification.

In the drawings accompanying the specification:

Fig. 1 illustrates a block of fused and crystallized silicon taken from the ingot;

Fig. 2 shows a cylindrical slab cut from the block of Fig. 1;

Figs. 3 and 4 disclose apparatus for polishing the surface of the silicon slab;

Fig. 5 shows a slotted boat or tray for holding

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the polished silicon slabs during their heat treatment;

Fig. 6 illustrates a heat chamber for treating the silicon slabs;

Fig. 7 shows an etchant bath for removing the oxidized coatings;

Fig. 8 illustrates the dissection of a slab into small wafers for use in the individual rectifying units;

Fig. 9 shows one of the wafers;

Fig. 10 shows a bath for etching the wafer after it is mounted; and

Fig. 11 discloses an assembled rectifier unit.

In the preparation and use of high-purity silicon material for ultra-high frequency purposes it has been found that its rectification performance and its electrical characteristics in other respects can be controlled to advantage by carefully selecting the impurities that are permitted to remain in the material and regulating the percentage in which they are present. For example, the conversion efficiency of the rectifier can be greatly enhanced by adding to the high-purity silicon material definite small percentages of elements such as boron. In general, however, it is found that as the percentage of the addition materials, which may be added for desirable reasons, increases there is a corresponding increase required in the duration of the heat treatment to which the crystalline material is finally subjected for the purpose of establishing the rectification surface. For instance, with certain amounts of boron added to the high-purity silicon, intervals of as much as five hours may be required for heat-treating the surface of the element. The longer the silicon slab is subjected to the heat treatment the greater the extent of diffusion of the impurities from the interior toward the surface, and therefore the longer the time required to effect the oxidation of these migrating impurities. Looking at it in another way, the longer the silicon slab remains in the oxidizing atmosphere the thicker becomes the coating of the oxide on the surface, resulting in a diminishing rate of oxidation relative to the rate of diffusion. With the continuous heat treatment method heretofore used for preparing the surfaces of these rectifying elements it has been difficult, if not impossible, to secure the most effective relationship between the diffusion of the impurities and their oxidation at the surface. With applicant's process, which will be presently described in detail, these difficulties are surmounted, and a high degree of control is attained over the relative rates of diffusion and oxidation.

One of the first steps in the process is the fusion and formation of the ingot. A suitable method for performing this step is disclosed in the application of H. C. Theuerer, Serial No. 517,060, filed January 5, 1944. If it is desired to include an addition material, such as boron, in the high-purity silicon ingot, a suitable method for this purpose is fully disclosed in the application of J. H. Scaff and H. C. Theuerer, Serial No. 545,854, filed July 20, 1944.

Following the casting of the ingot, a block 1 is cut from any desired part thereof, following which the block 1 is cut into thin slabs, such as the slab 2. Diamond saws are usually employed for this purpose, and good results are obtained when the large surface of the slab is normal to the axis of the ingot.

The next step in the preparation of the slab 2 is to polish one of its large faces to a high finish. To accomplish this step the slab 2 is cemented to

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a flat steel block 3 with a suitable thermoplastic cement. The exposed surface of the slab 2 is then polished by rubbing it over the surface of an abrasive paper 4 secured to a flat plate 5, the paper 4 being changed from one degree of fineness to another as the process proceeds. If desired, the polishing surface may be lubricated with a mixture of light oil and kerosene. The final step in the polishing operation is performed by applying the slab 2 to a rubbing lap 6 having its surface covered with polishing paper 7 of extreme fineness. During this operation the slab 2 is pressed against the polishing surface with a definite force and is moved in a circle eccentric to the lap 6 and in the direction opposite to the direction of rotation of the lap. During the wet stage of the polishing a scum of fine particles of silicon suspended in the lubricant forms over the surface of the slab. As the process proceeds the scum dries and distributes itself over the surface of the lap to form the final polishing medium. Once this surface is formed a very few seconds of additional polishing are necessary to produce a high finish on the surface of the slab. The slab is now removed from the block 3 and cleaned.

The next step in the preparation of the slab 2 is to oxidize the polished surface thereof. To this end a plurality of polished slabs are stacked in pairs in the notches 8 formed in the sides of a tray or boat 9 of some refractory material. The pairs of slabs are placed in their respective slots with the unpolished surfaces back to back and the polished surfaces fully exposed to the surrounding atmosphere. Next the boat 9 is placed in the furnace for the first short heat run.

The furnace used may be of any suitable type, one of which is illustrated in Fig. 6. It includes a quartz tube 10 of suitable diameter surrounded by a cylindrical jacket 11 of any suitable refractory material and a heat winding 12 disposed about the exterior of the cylindrical jacket 11. The ends of the tube 10 are closed by plugs 13 and 14 of suitable material which are sufficiently removed from the heating zone to suffer no appreciable deterioration. The plug 13, which may be left permanently in place, carries a thermocouple 15 and associated indicating scale 16 for determining the temperature within the furnace. Also the plug 13 carries a pipe 17 communicating with the interior of the furnace. The plug 14 at the opposite end of the tube 10, which is removed to admit the boat 9 with its charge of slabs for each heat run, is also equipped with a communicating tube 18. Through these tubes 17 and 18 the desired atmospheric conditions are maintained within the heating chamber. Power for generating the heat in the coil 12 is supplied from a suitable source 19 over a circuit including the thermocouple and a controlling switch 20.

The duration of the heat run may be varied according to the characteristic of the material being treated and according to the final results required. As an illustration, however, it will be assumed that the first run continues for a period of one hour and fifteen minutes at a temperature of 1000° C. During this relatively short interval the oxidation of the impurities at and near the exposed polished surfaces of the slabs 2 takes place at a high rate. That is to say, these impurities are withdrawn from the thin surface layer by oxidation at a rate faster than they can be replaced by the diffusion of like impurities within the interior of the body. As the oxidation proceeds a thin coating of the oxide is formed on

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the surface, and at the end of the run the charge is removed from the furnace and the slabs are permitted to cool to room temperature.

Next the oxidized slabs 2 are immersed in an etchant bath 21 contained in a suitable tray or dish 22. The etchant may comprise a mixture of hydrofluoric acid and water in the proportion of one part of acid to four parts of water by volume. At the end of a suitable interval, say five minutes, the slabs are removed from the bath, at which time the etchant has completely removed the oxide coating on the surfaces thereof.

Next the etched slabs 2 are again stacked in the boat 9 and placed in the furnace for the second heat run. This second run, like the first, may be varied in duration if desired. For the purpose of the present description however, it will be assumed that it too is continued for a period of one hour and fifteen minutes at a temperature of 1000° C. During the second run the partially conditioned surface of the silicon slab is again subjected to a high rate of oxidation of the impurities in the surface layer, with the result that this layer is rendered substantially free of oxidizable impurities. Following the second run the slabs are removed from the furnace and permitted to cool. If desired they may be etched as before and returned to the furnace for another short run. It will be assumed, however, that two of these short heat treatments are sufficient.

After the slab 2 with its multiple heat treated surface has been permitted to cool, the opposite side thereof is ground to remove any oxide coating that may have accumulated thereon and is then plated with nickel. The slab 2 is then cut into small wafers 23 of dimensions suitable for use in the rectifier assemblies. The wafer 23 thus prepared is soldered with its nickered surface to the threaded stud 24 of the metallic base 25, Figs. 10 and 11. Following the soldering of the wafer to the threaded stud of the base member and before the rectifier unit is assembled, as seen in Fig. 11, the final oxide layer covering the polished upper surface of the wafer 23 is removed by etching the entire base assembly in a bath 26 of hydrofluoric acid and water. After the oxide layer has been removed, the base member 25 is screwed into the ceramic cylinder 27. In a similar manner, stud 28, which is integral with the metallic cap 29, is firmly screwed into the opposite end of the cylinder 27. The cap 29 contains a central bore for receiving the cylindrical metallic contact holder 30. The set screws 32 are tightened to seize the holder 30, and the holder is adjusted until the tip end of the tungsten wire 31, the opposite end of which is soldered to the holder, makes contact with the polished surface of the wafer 23 and the desired degree of force has been applied to the contact engagement of the wire 31 with the silicon wafer 23. The unit is then tapped lightly on its side until the desired characteristic is obtained.

Although a method has been described herein in considerable detail for heat treating translating materials, such as crystalline silicon, it will be understood that the invention may be applied to the treatment and preparation of other materials, that addition materials other than those mentioned may be included in the crystalline bodies of silicon or other material, and that many variations may be made in the details of the method described.

What is claimed is:

1. The method of making a translating element for electric waves of high frequency which

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comprises forming a crystalline body of high-purity silicon having definite predetermined electrical characteristics, and subjecting said body to a plurality of separate and successive heat treatments to form in the surface thereof a thin layer having electrical characteristics which differ from those of the remaining part of said body.

2. The method of making a translating element for electric waves of high frequency which comprises forming a crystalline body having definite predetermined electrical characteristics, subjecting said body to separate and successive heat treatments to form on the surface thereof an oxide coating and a thin underlying layer having electrical characteristics which differ from those of the remaining part of said body, and removing said oxide coating.

3. The method of making a translating element for electric waves of high frequency which comprises forming a crystalline body of high-purity silicon having definite predetermined electrical characteristics, subjecting said body to separate and successive heat treatments to form on the surface thereof an oxide coating and a thin underlying layer having electrical characteristics which differ from those of the remaining part of said body, and removing said oxide coating after each heat treatment.

4. The method of making a translating element for electric waves of high frequency which comprises forming a crystalline body having definite predetermined electrical characteristics, subjecting said body to separate and successive heat treatments to form on the surface thereof an oxide coating and a thin underlying layer having electrical characteristics which differ from those of the remaining part of said body, and removing said oxide coating with an etchant.

5. The method of making a translating element for electric waves of high frequency which comprises forming a crystalline body of high-purity silicon having definite predetermined electrical characteristics, subjecting said body to separate and successive heat treatments to form on the surface thereof an oxide coating and a thin underlying layer having electrical characteristics which differ from those of the remaining part of said body, and removing said oxide coating with an etchant solution containing hydrofluoric acid.

6. The method of making a conducting element for electric waves which comprises forming a crystalline body having a definite small percentage of impurities therein, and subjecting said body to a plurality of separate and successive heat treatments, each of which is of a duration that causes the oxidation of the impurities in the surface of said body at a rate exceeding the rate of diffusion of the impurities within the body toward said surface.

7. The method of making a conducting element for electric waves which comprises forming a crystalline body of silicon having a definite small percentage of impurities therein, subjecting said body to a plurality of separate and successive heat treatments, each of which causes the oxidation of the impurities in the surface of said body at a rate exceeding the rate of diffusion of the impurities within the body toward said surface, and removing after each heat treatment the oxide formed on the surface of said body.

8. The method of making a conductive element which comprises forming a crystalline body containing a small percentage of impurities and sub-

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jecting said body to a plurality of successive heat treatments, each comprising diffusioning impurities toward the surface of the body and simultaneously oxidizing said impurities at said surface, the duration of each heat treatment being such that the rate of oxidation of impurities at the surface exceeds the rate of diffusion of impurities to said surface.

9. The method of making a conductive element for electric waves that comprises forming a crystalline body having a small percentage of impurities therein, heat treating the body to oxidize its surface and simultaneously to cause migration of impurities toward said surface, stopping the heat treatment while the rate of oxidation of impurities is greater than their rate of migration, removing the oxidized material, and repeat-

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ing the heat treatment and removal of oxidized material until the layer whose surface is exposed is sufficiently free of impurities.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,640,335	Grondahl	Aug. 23, 1927
1,649,744	Rüben	Nov. 15, 1927
1,781,088	Strobel	Nov. 11, 1930
1,743,160	Presser	Jan. 14, 1930
2,137,316	Van Geel et al.	Nov. 22, 1938