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ALLOY AND COMPOSITE STOCK

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This invention relates to alloys and to composite stock incorporating these alloys, these alloys and the composite stock being useful in forming components of solid-electrolyte batteries.

The components of this type of battery are, in many cases, formed by a layer of silver adhered to a layer of a silver halide selected from the group consisting of silver iodide, silver bromide and silver chloride. The silver layer acts as the anode of the battery, and the silver halide layer as the electrolyte thereof. The silver halide layer can be formed by heating a section of silver in an atmosphere of the halide vapor whereby the exposed surface of the silver becomes tarnished with a layer of the silver halide. The surface of the silver layer opposite that to which the silver halide layer is adhered can be bonded to a base layer of corrosion-resistant metal such as stainless steel preferably of the austenitic type, Monel and Inconel. Monel is a line of high nickel-copper alloys and Inconel is a high nickel-chromium-iron alloy; both of these being registered trademarks of the International Nickel Co., Inc., of New York, New York.

Among the difficulties which present themselves in providing the components of a battery of the above-described type, is that of obtaining a satisfactory degree of adherence between the silver halide layer and the silver layer. Also, it is important, in many cases, that any modification of the silver layer to improve the adherence between the latter and the silver halide layer not have the effect of preventing or deterring the formation of an adequate bond between the silver layer and the corrosion-resistant, metal, base layer.

Accordingly, an object of this invention is to provide new and improved alloys and composite stock incorporating said alloys, these being useful in forming components of a solid-electrolyte battery.

A further object of this invention is to provide such alloys which exhibit improved adherence to silver bromide, silver iodide and silver chloride.

A further object is to provide such composite stock which includes a layer of one of said silver halides and an improved silver alloy layer, the two layers having improved adherence therebetween.

A further object is to provide such an alloy and such composite stock capable of being mechanically worked without deleterious effect.

Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly comprises the elements, combination of elements, features of structure, arrangements of parts, the ingredients, combinations of ingredients, the proportions thereof, and features of composition which will be exemplified in the structures and products hereinafter described, and the scope of the application of which will be indicated in the following claims.

According to this invention, an improved silver-base alloy is substituted for the above-mentioned pure silver layer, the silver-base layer consisting essentially of from an effective trace to 0.75% by weight of cobalt, from 0% to 0.15% by weight of copper and the remainder silver. No perceptible improvement in the adherence between the silver halide layer and the silver-base alloy layer (due to the presence of the cobalt) has been detected when the percentage of cobalt in the latter layer was less than

0.05%, and this is, therefore, what is meant by the term "effective trace" as used herein. The upper limit of 0.75% by weight of cobalt as set forth herein is determined by the fact that this is the highest percentage of cobalt attainable in the alloy. In this regard, the alloy of this invention is produced by conventional melting and mixing techniques, and when an excess of 0.75% of cobalt is melted and mixed with silver, all of the excess cobalt rises to the surface of the melt.

The addition of cobalt to silver, the former within the range of from an effective trace to 0.75% by weight, substantially improves the adherence thereto of the silver halide layer. The magnitude of this improved adherence is evidenced by back and forth bending and creasing of a strip of composite stock formed by heating a strip of the silver-base alloy of this invention in an atmosphere of iodine vapor to provide a layer of the silver-base alloy tarnished with a layer of silver iodide. When this composite stock is so bent and creased, there is no flaking or other damage to the silver halide layer, the two layers otherwise remain intact, and these layers remain uniformly adhered to each other. In contradistinction thereto, a layer of pure silver provided with an adhered layer of silver iodide by tarnishing in the manner described above does not exhibit these improved qualities. This improved adherence is important for the reason, among others, that the composite material should be capable of being provided in strip form and subsequently worked (such as by stamping out pieces from the strip) without damage to the composite stock. Best results from the standpoint of effective adherence at a minimum cost are obtained when the percentage by weight of the cobalt in the alloy is 0.20.

The improved results noted above with respect to the addition of cobalt to the silver-base alloy are obtained whether or not copper in a range up to 0.15% by weight is incorporated into the alloy. It has been found, however, that when copper is included in the range of up to 0.15% by weight, an even better adherence between the silver halide and the silver-base alloy layers is obtained, along with an improvement in the quality of the bond between the silver-base alloy layer and the base metal layer.

It will be understood that the silver base alloy according to this invention includes cobalt with or without copper, both in the above-stated percentage ranges, and the remainder silver except for the inclusion of impurities and agents which do not deleteriously affect the alloy in the environment of a solid-electrolyte battery or in the environment of other electrical applications (such, for example, as transistors). An example of an agent which can be incorporated into the silver halide layer is cadmium bromide as disclosed in U.S. Patent Re. 24,408 to A. J. Hack et al. Conventional commercially fine silver or "three nines" fine silver is well suited for the addition thereto of cobalt in the percentage range stated above to provide an improved alloy according to the invention, it being noted that ordinarily this material incorporates a quantity of copper within the percentage range named above. The impurities present in commercially or "three nines" fine silver have been found to have no ill effect on the silver alloy of this invention.

Theorizing, it is believed that these improved results may be accounted for, at least in part, as follows. First, cobalt is practically insoluble in silver, and when alloyed therewith the cobalt precipitates out at the boundaries of the silver grains. When an alloy of this invention consisting essentially of silver and cobalt is heated in an atmosphere of halide vapor, the chemical reaction of the halide with the silver in the alloy layer is promoted and proceeds along the grain boundaries at a faster rate (as compared, for example, with pure silver) due to the presence of the cobalt. Additionally, cobalt acts as a grain-

growth inhibitor whereby advancement of the chemical reaction along the grain boundaries is enhanced due to the presence of more and finer grains of the silver.

The interface between two layers formed by tarnishing a layer of pure silver in an atmosphere of iodine is smooth as compared with the interface resulting from so tarnishing, for example, a layer of "three nines" fine silver which contains a significant amount of copper less than the maximum of the range for copper according to this invention (and an insignificant, if any, amount of cobalt). It is believed that this indicates the effect of an alteration of the silver by the copper similar to that as theorized above with respect to cobalt with the result of apparently an even greater degree of preferential grain boundary attack by the halide. Whatever the mechanics of the cause may be, the effect of incorporating copper along with cobalt in the silver as described above is further to increase the degree of adherence between the layers.

In any case, the result of the preferential grain boundary attack by the halide, absent or present the copper, is a multitude of microscopic anchors extending along the grain boundaries into the silver-alloy layer from the silver halide layer; these anchors being responsible, in part, for the improved adherence between the two layers. Also, due to the rough interface resulting between the two layers, the interfacial area is increased correspondingly increasing the degree of adherence therebetween. The presence of the above-described "anchors" and rough interface is apparent by examination of metallographically prepared transverse cross-sections of the composite stock of this invention.

In forming a composite article comprising an intermediate layer of the silver-base alloy according to this invention adhered at one surface to a layer of one of silver iodide, silver chloride and silver bromide, and bonded at its opposite surface to a layer of corrosion-resistant metal, the latter is solid-phase bonded to the silver-base alloy layer by the method disclosed and claimed in U.S. Patent No. 2,691,815 granted on October 19, 1954, to Boessenkool et al. By way of example, a length of the above-identified silver-base alloy according to this invention is so solid-phase bonded to a length of corrosion-resistant metal such as austenitic stainless steel, this composite is then rolled to the desired gauge with intermediate annealing steps, if necessary, and the silver halide layer is formed on the exposed surface of the silver-base alloy layer by heating the composite and exposing it to an atmosphere of the respective halide vapor. It has been found that when the silver base alloy layer incorporates copper as well as cobalt, all as described above, the advantage of an even greater adherence between the silver-base alloy and the silver halide layers results along with the added advantage that the quality of the bond between the silver-base alloy layer and the corrosion-resistant, metal, base layer is improved.

It is to be noted that the layer of silver halide can be provided in adhered relation to the anode-forming layer in producing the composite stock according to this invention by methods other than tarnishing as described above. By way of example, the alternative methods disclosed in U.S. Patent No. Re. 24,408 to A. J. Hack et al. could be used.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As many changes could be made in the above constructions without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. Composite stock comprising a layer of a silver selected from the grounp consisting of silver iodide, silver bromide and silver chloride adhered to a layer formed of an alloy consisting essentially of from 0.05% to 0.75% by weight of cobalt, up to 0.15% by weight of copper, and the remainder silver.

2. Composite stock comprising a layer of silver iodide adhered to a layer formed of an alloy consisting essentially of from 0.05% to 0.75% by weight of cobalt, up to 0.15% by weight of copper, and the remainder silver.

3. Composite stock comprising a layer of a silver halide selected from the group consisting of silver iodide, silver bromide and silver chloride adhered to a layer formed of an alloy consisting essentially of 0.20% by weight of cobalt and the remainder silver.

4. Composite stock comprising an intermediate layer formed of an alloy consisting essentially of from 0.05% to 0.75% by weight of cobalt, up to 0.15% by weight of copper and the remainder silver; said intermediate layer being adhered at one surface thereof to a layer of a silver halide selected from the group consisting of silver iodide, silver bromide and silver chloride; and said intermediate layer being bonded at the opposite surface thereof to a corrosion-resistant, metal, base layer.

5. Composite stock comprising an intermediate layer formed of an alloy consisting essentially of from 0.05% to 0.75% by weight of cobalt, up to 0.15% by weight of copper and the remainder silver; said intermediate layer being adhered at one surface thereof to a layer of silver iodide; and said intermediate layer being bonded at the opposite surface thereof to a corrosion-resistant, metal, base layer.

6. Composite stock comprising a layer of a silver halide selected from the group consisting of silver iodide, silver bromide and silver chloride adhered to a layer of an alloy consisting essentially of from 0.05% to 0.75% by weight of cobalt and the remainder silver.

7. The composite stock as set forth in claim 6 wherein said alloy layer is bonded to a corrosion-resistant, metal, base layer.

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