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ACID RESIST POWDER FOR USE IN ETCHING

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This invention relates to a composition of matter for use in etching, and with regard to certain more specific features, to a composition of matter in powder form adapted to be used as an acid resist powder in the etching steps of photo-engraving and like processes.

This application is in part a continuation of my application Serial No. 72,061, filed April 1, 1936, and entitled "Composition of matter for use in etching."

Among the several objects of the invention may be noted the provision of a composition of matter of the class described which is of predictably uniform characteristics throughout successive batches, and which is compounded from ingredients of predictably uniform characteristics; a composition of matter of the class described which, when used as an acid resist powder in the etching of photo-engraving plates and the like, has such characteristics as the ability to adhere satisfactorily to the metal of the plate, particularly after "burning in" the plate, but which, at the same time, may be brushed on the plate in such manner that it does not adhere where it is not wanted; a powder which bakes or "burns in" on the metal plate to provide a satisfactory acid-resisting coating, but which at the same time has no tendency to flow while heated upon the plate; a powder which is water-repellent, and which is acid-proof; a powder which, upon heating or "burning in", changes color sufficiently so that the operator will know when a satisfactory temperature has been reached; and the provision of a composition of matter of the class described which is economically compounded from relatively inexpensive ingredients. Other objects will be in part obvious and in part pointed out hereinafter.

The invention accordingly comprises the elements and combinations of elements, and features of composition, which will be exemplified in the products hereinafter described, and the scope of the application of which will be indicated in the following claims.

The product heretofore used by substantially all photo-engravers as an acid resist powder has been one based primarily on a natural resin mixture called dragon's blood. The composition and quality of dragon's blood resin, since it is a natural product collected over widely distributed regions of the world, have been notably lacking in uniformity. Because of this lack of uniformity, it has been the custom to subject the dragon's blood to a preliminary process of purification. The partially purified resin is subsequently,

through blending or the addition of mineral fillers, brought to a proper working consistency. Even then, however, successive batches of this product lack the characteristics of uniformity which are desired. These modified powders made from natural dragon's blood resin are known commercially as "dragon's blood", and will be so referred to hereinafter.

The present invention may be designated as an artificial substitute for dragon's blood, in that it affords all of the necessary physical properties of dragon's blood which render it particularly adaptable for use as an etching powder. Its chemical composition, on the other hand, is not in any way related to dragon's blood. Each component is selected with respect to its adaptability to produce a desired physical effect in the properties of the powder without regard to the chemical composition of such component. A product of this nature offers great advantages over natural dragon's blood by reason of the fact that, being made from substances of known composition, succeeding batches can be compounded with the utmost uniformity. It also has the advantage that powders of slightly varying properties, such as adhesiveness, "burning in" temperature, etc., which are adaptable to different types of etching work, can easily be synthesized by slightly varying the proportions of the essential ingredients.

Broadly speaking, the composition of the present invention comprises five ingredients, which may be enumerated as follows:

Resinaceous material
Filler material
Adhesion powder
Lubricant powder
Coloring material.

The characteristic function of each of these several ingredients will be discussed in detail hereinafter.

The resinaceous material to be used is chosen with respect to its physical characteristics. It may be either a single resin or wax, of either natural or synthetic origin, or it may be a mixture of two or more such natural or synthetic products, so compounded as to afford the satisfactory working properties hereafter set forth. The term resinaceous material wherever used is intended to refer to such a resin or wax, or, to a mixture of such resins or waxes. These desirable physical characteristics for the resinaceous material for the present invention may be enumerated as follows:

1. It should be water repellent.
2. It should be acid resistant.
3. It should be substantially free from volatile components.
4. It should not oxidize readily in the air, even when exposed to atmospheric conditions in a finely powdered form.
5. It should be sufficiently friable, so that when mixed with the filler, the mixture may be pulverized to a very fine powder.
6. It should not be gummy or tacky, even at extreme summer temperatures.
7. It should have a softening point of 65° to 95° C. The most satisfactory softening point is believed to be 76° to 81° C.
8. It should have the property of completely fusing to a liquid state with a small increase in temperature above the initial softening point.
9. It should have the foregoing eight physical characteristics in reproducible fashion. By this is meant that the resinaceous material should be of a definite composition throughout successive batches or successively obtained supplies, so that it may be relied upon to supply the foregoing characteristics in a uniform manner. While natural dragon's blood, for example, may fulfill all of the foregoing characteristics, because it occurs in nature as a mixture of several components which are present in varying proportions, it is not of reliably uniform composition, and its characteristics vary with successive batches, so that it cannot be used as the resinaceous material of the present invention without sacrificing the desirable advantage of uniformity of characteristics.
- A resinaceous material which has been found to meet all of the foregoing requirements and hence one which is highly satisfactory in the composition of matter forming the present invention, is a mixture of approximately 1 part carnauba wax, having a softening point of 69° to 70° C., with approximately 4 to 5 parts of a synthetic phenolic base resin product, which may be made according to the following procedure:
- In a five-liter round bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer, place 1200 grams p-tertiary amyl phenol, and 500 grams aqueous formaldehyde (37½% CH₂O). Heat the mixture to 98° C., and then add, cautiously, 12 grams of concentrated hydrochloric acid. Then reflux the mixture for three hours, during which time most of the formaldehyde combines and a resin is formed. Then connect the flask to a condenser for distillation, and place a thermometer in the liquid resin. Distill off the water and hydrogen chloride by heating the flask directly with a flame. After the water has been removed, continue heating until the temperature of the liquid resin reaches 200° C. Maintaining this temperature, remove the unreacted p-tertiary amyl phenol by applying a vacuum of 26" to the flask. The molten resin may then be dumped into a metal container and allowed to cool, and subsequently pulverized to the required extent. The resulting synthetic resin has a softening point of approximately 83½° C.
- The mixture of 4 to 5 parts of this synthetic resin and 1 part of carnauba wax, which mixture is a suitable resinaceous material for the purposes of the present invention, has a softening point of 76° to 78° C., and possesses the other necessary characteristics specified.
- The synthetic resin described above can be replaced, with certain advantages in cost economy,

by a synthetic resin manufactured by General Plastics, Incorporated, North Tonawanda, New York, and sold under the trade name "Durez S-5758". I am informed that said "Durez S-5758" resin is a phenol-formaldehyde resin of the thermoplastic type modified with a resin plasticizer manufactured and sold by Monsanto Chemical Co. under its trade name "Santicizer B-16". This last-named plasticizer is the substance butyl phthalyl butyl glycolate, and it is described at length, together with the manner in which it is used to plasticize resins, in an article by T. S. Carswell and Arnold Kilpatrick in "Plastic Products" for November, 1933, under the title "A new group of plasticizers". Sufficient plasticizer is added to and worked into the thermoplastic phenol-formaldehyde resin to bring the melting point of the resin to the proper value. In making the melting point determinations two points are observed and the following specifications are adhered to:

	°C.
Shrink point-----	80-81.5
Clear point-----	88-91.5

The color specification, which is determined by comparing with the Barrett color specification standard, is C-7 to C-8. The resin is of the oil soluble type and is not heat reactive. The resin is perfectly clear and amber in color. The mixture resulting from the compounding of the carnauba wax and the "Durez S-5758" resin has a softening point of 79 to 81° C. and possesses the other necessary characteristics as specified.

Carnauba wax, mentioned above, is a natural product obtainable commercially in uniform quality.

By reason of the fact that the method of determining the softening point of resins has not been generally established, the method to which the foregoing temperatures are correlated is described briefly as follows: The resin is finely powdered and filled into a dry capillary tube, which is sealed at one end. The tube is then immersed in an oil bath which is heated at such a rate that the temperature of the bath increases at the rate of approximately 2° C. per minute. The softening point is defined as the temperature at which the finely powdered resin particles appear to pull away from the walls of the capillary tube, when thus heated.

It is to be noted that physical characteristics, rather than chemical ones (except insofar as the chemical characteristics affect or determine the physical characteristics), determine the suitability of the resinaceous material for the purposes of the present invention. If the physical characteristics of a resinaceous material are suitable, then its chemical composition is of little moment. It so happens that of the resins I have investigated, the thermoplastic phenol-formaldehyde resins appear generally to be most suitable, but this is to be interpreted as merely indicating only one type of resin that is suitable, and not as excluding resins of other compositional characteristics that are also suitable by reason of their conformation to the stated physical characteristics. The terms "suitable resinaceous material" are accordingly hereinafter to be understood as defining a material having substantially all the foregoing desired physical characteristics.

The second primary ingredient comprises the filler or pigment material. The principal purpose of this material is to afford a body to the finished product, so that when heated on a plate to the softening point of the resin, the layer of powder

retains substantially its original form and position without spreading or flowing over the surface of the plate. The filler should have the further property of being reasonably water-repellent and acid-resistant, so that when exposed to the solutions used in etching, the solutions will not penetrate through the powdered portions and thus attack the plate in these areas which it is desired to protect. These characteristics should be found when the filler material is pulverized to such an extent that it all passes through a one hundred mesh screen and the greater proportion passes through a two hundred mesh screen, in which fineness it is desirably used in the present composition.

Suitable filler material for the present composition include mineral materials such as soapstone, which when pulverized to the extent stated, has a somewhat micaceous structure, and which is highly water-repellent even in such fineness. Another suitable filler material comprises the natural mineral natine, or uncalcined vermiculite, which when calcined is sold as the heat insulating product "Zonolite."

Another suitable filler material comprises thoroughly cured synthetic resins of the phenol aldehyde type, such as are frequently used for molded bottle caps and the like. Many of these cured resins possess the necessary physical properties adaptable to a suitable filler and do not substantially soften at the temperature employed in "burning in" the powder. By reason of their high melting point, they behave substantially as inert ingredients or fillers. In some instances, however, such a resinaceous filler will act in use somewhat as a combined resinaceous material and filler material, particularly if the operator uses high enough temperatures in "burning in" the powder.

The terms "suitable filler material" will be used hereinafter to define a filler material having substantially all the foregoing desired characteristics.

The resinaceous and filler components, when compounded in the proper manner, comprise the essential constituents of the present invention. Without these two constituents no satisfactory composition can be made for the desired purpose. In order to still further enhance the working properties of the powder, auxiliary or secondary ingredients are highly desirable, as will appear from a description hereinafter of the functions of each of such ingredients. It is to be understood, however, that these secondary components are not indispensable ingredients and they may be dispensed with or other substances may be substituted which have similar properties, without materially impairing the working properties of the composition.

The first secondary ingredient may be designated as an "adhesion powder." The terms "adhesion powder" when used in this respect are intended to designate an ingredient which imparts to the finished composition the property of adhering to the vertical surfaces or shoulders of a partially etched plate, when the powder is brushed against these surfaces under the conditions ordinarily encountered in the usual process of etching.

The adhesive property here referred to is not essentially dependent upon tackiness or gumminess. The adhesion powder used is, on the other hand, similar in behavior to such powders as possess the property of adhering to perfectly dry surfaces by reason of their electrostatic charge.

It has not been definitely established that the adhesive powder described owes its beneficial function entirely to the electrostatic charge which it develops on being brushed over the plate, but this example is used as describing the type of powders which function satisfactorily in this respect.

In the present invention, the metallic stearates and particularly aluminum stearate function very satisfactorily in affording this adhesive property. Another suitable substance which affords this same property is thymol iodide. The terms "adhesion powder" as used herein are accordingly defined as meaning light, fluffy powders which adhere readily to dry surfaces against which they are brushed in a manner similar to or identical with those powders which adhere by reason of an electrostatic charge, as contrasted with adhesion materials which adhere by reason of a gummy or tacky texture.

The second secondary ingredient comprises the lubricant powder. The purpose of this powder is to provide a lubricant material for the other ingredients so that when they are brushed on the etched plate, the powder as a whole is prevented from sticking to the plate where it is not wanted. Some resinaceous materials exhibit a tendency to adhere to the flat, partially etched portions of the plate where they are not wanted. By the addition thereto of a lubricant powder of the desired properties, this tendency is satisfactorily counteracted, so that when the powder is brushed on to the partially etched plate it adheres firmly to the vertical sides or shoulders, and, at the same time does not adhere to the flat or horizontal areas of such partially etched plate, thus leaving such flat areas exposed to the free action of the etching solution.

Powdered mineral talc has been found to be eminently satisfactory as a lubricant powder. This powder should be capable of passing a two hundred mesh or finer screen. Talc, it will be understood, is a well-defined mineral substance of uniform characteristics, comprising a magnesium aluminum silicate.

Other lubricant powders than talc may be used, providing they have the desired characteristics enumerated.

The third secondary ingredient comprises a coloring material. The purpose of this material is to impart to the composition a color whereby it can readily be distinguished when it is in position on a plate. It will be understood that the necessity for this coloring material, as an additional ingredient, depends upon the color of the composition as it is obtained prior to the addition of the coloring material. If the ingredients heretofore named specifically are used, the color of the composition is an orange-brown, which does not show up readily on the zinc plates customarily used, so that the addition of a coloring material is desirable. A further function of the coloring material, if suitably selected, is that it will indicate by a change in its color when the powder has been sufficiently "burned in" on the plate.

Another advantage of the increased visibility afforded by the coloring material is in enabling the etcher to determine the end of the "bite", that is, that point at which the protective coating has been removed from the shoulders by the action of the etching solution, so that the shoulders are exposed to the action of the solution, rendering it necessary that the plate be re-powdered before proceeding further with the etching.

Suitable coloring materials include both pig-

ments, such as ferric oxide and dyes, such as the commercially available dye known as "oil-soluble red." The last-named dye is the preferred coloring material for use with the other specific ingredients mentioned above. It has the advantage of changing from a light red to a clearly distinguishable dark red when the powder is "burned in" on the plate.

Whatever coloring material is used, in order for it to be most satisfactory, it should not bleach either through the action of heat or through acid treatment. It is not necessary that the coloring matter be red, since any coloring matter which renders the powder readily visible and which has the further property of changing its color during the "burning in" process would be satisfactory for this purpose.

It is to be understood that the coloring matter does not perform any essential function in the working properties for the composition but is added merely for the purpose of providing a contrast in color, so that the powdered portions may be readily distinguished from the unpowdered areas.

The term "suitable coloring material" is used hereinafter to define a coloring material which conforms approximately to the above-stated characteristics.

The proportions of the foregoing primary and secondary ingredients in the composition of matter of the present invention may vary widely, depending upon the particular ingredients selected. However, satisfactory proportions will usually be found to be included within the following ranges:

	Per cent by weight
Resinaceous material.....	24-32
Coloring material.....	$\frac{1}{2}$ -1 $\frac{1}{2}$
Adhesion powder.....	2-4
Lubricant powder.....	4-7
Filler material.....	Balance

The following two specific formulae give proportions, covering a range within which the ingredients heretofore named specifically, when properly compounded and pulverized, yield products in the form of powders which are satisfactory for the stated purposes:

	Formula 1	Formula 2
	Percent	Percent
Resin (the synthetic resin heretofore described, or the aforesaid "Durez S-5758").....	21.0	21.0
Wax (carnauba).....	5.2	6.0
Coloring matter ("oil-soluble red dye").....	.8	.9
Adhesion powder (aluminum stearate).....	2.6	3.0
Lubricant powder (talc).....	5.2	6.0
Filler (micaceous mineral).....	65.2	60.1
Total.....	100.0	100.0

The proportions of the several ingredients may be varied both within and outside the limits set by the above two specific examples, as well as the range formula heretofore given, without seriously impairing the usefulness of the product.

The amount of inert filler material will vary inversely as the density of such filler material, because the filler material is intended to comprise a certain portion of the total volume of the various ingredients employed, so that in the case of lighter powders, a less amount is needed than in the case of heavier materials.

The order of mixing the several ingredients of the product is important, although not absolutely necessary to the obtaining of a satisfactory product. An order of mixing which has been found

to be particularly advantageous is the following:

The resinaceous material is first melted. If, as in the foregoing specific formulae, the resinaceous material comprises a mixture of a resin and a wax, the melting is accompanied by a thorough intermixing of the ingredients of the mixture. To the liquid is then added the coloring material, particularly if it be in the form of a dye, and this is likewise stirred thoroughly until the dye is dissolved in the molten resin, or if a pigment is employed until all of the pigment is thoroughly and uniformly incorporated in the molten resin. Then part of the filler material is added, with sufficient stirring to make the mixture uniform. It will be found that most of the filler material (such as 75% of it), or even all of it, depending upon the mixing equipment used, may be added to the liquid without destroying its ability, to be worked. It is desirable that all, or at least a large portion, of the filler material be added at this time. The mixture thus prepared is allowed to cool and set, after which it is crushed to the form of fairly coarse particles (such as, for example, those capable of passing a four mesh screen), after which the remainder of the filler material, if any, and the remaining ingredients are added. The entire mixture is then reduced to a fine powder in a suitable mill or pulverizer. Pulverization is continued until all of the powder is capable of passing a one hundred mesh screen, for example, and the majority of the powder is much finer.

The degree of fineness of the finished powder has some influence on its working properties. If the particles be too coarse, they do not adhere satisfactorily to the shoulders of the plate and furthermore may afford an uneven surface. If, on the other hand, the entire portion of the powder be reduced to too fine a state of subdivision, it tends to become very dusty and is also open to the objection that it exhibits a tendency to "drag" or adhere to any slightly roughened surfaces. For these reasons, it has been found that powders having such a fineness that the coarser particles are of approximately 100 mesh and which contain a considerable portion of finer powder ranging in the neighborhood of 300 mesh, seem to work most satisfactorily for ordinary etching purposes.

By mixing a large portion of the filler material into the melted resin as specified, it is found that, in the finished product, the majority of the particles of filler material are completely coated with the resinaceous material. This is distinctly advantageous, as it results in a proper adhesion of the powder when it is "burned in" on the plate, in such manner that the filler particles are contacted with and embedded in a matrix of resin at all points. When the resinaceous material is ground or pulverized separately and the filler is then added, without the two being melted together, it is sometimes found that there is a separation on the plate to the extent that the filler particles are no properly bound to the plate by the resinaceous particles when the melting or "burning in" is done.

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 carrying out the above compositions 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.

I claim:

1. An acid resist powder comprising the following ingredients in approximately the stated proportions:

Per cent

5	Resinaceous material.....	24-32
	Lubricant powder.....	4-7
	Adhesion powder.....	2-4
	Coloring material.....	1/2-1 1/2
	Filler material.....	Balance

10 2. A composition of matter as set forth in claim 1 in which the resinaceous material includes a thermoplastic phenol-formaldehyde synthetic resin.

15 3. A composition of matter as set forth in claim 1 in which the resinaceous material includes thermoplastic phenol-formaldehyde synthetic resin, and a wax substantially of the characteristics of carnauba wax.

20 4. A composition of matter as set forth in claim 1 in which the resinaceous material includes a thermoplastic phenol-formaldehyde synthetic resin, and a wax substantially of the characteristics of carnauba wax, and the filler material comprises a finely pulverized micaceous mineral.

25 5. An acid resist powder as set forth in claim 1, in which the lubricant powder consists of talc.

6. An acid resist powder as set forth in claim 1, in which the adhesion powder consists of a metallic stearate.

7. An acid resist powder including the following ingredients in approximately the stated proportions:

Per cent

Suitable resinaceous material.....	30.0	5
Mineral filler material.....	60.1	
Talc.....	6.0	
Aluminum stearate.....	3.0	
Coloring material.....	0.9	

8. An acid resist powder including the following ingredients in approximately the stated proportions:

Per cent

Resinaceous material.....	26.2	
Filler.....	65.2	15
Talc.....	5.2	
Aluminum stearate.....	2.6	
Dye.....	0.8	

9. An acid resist powder comprising of the order of one-fourth to one-third resinaceous material, one-half to three-fourths filler material, and one or more of the following secondary ingredients in the proportion stated:

Per cent

Lubricant powder.....	4-7	25
Adhesion powder.....	2-4	
Coloring material.....	1/2-1 1/2	

DONALD B. ALNUTT.

Disclaimer

2,168,756.—*Donald B. Almutt*, St. Louis, Mo. ACID RESIST POWDER FOR USE IN ETCHING. Patent dated Aug. 8, 1939. Disclaimer filed Jan. 7, 1950, by the inventor; the assignee, *Mallinckrodt Chemical Works*, joining and assenting.

Hereby enters this disclaimer to claims 1, 2, 3, 4, 5, and 9 of said patent.
[*Official Gazette January 31, 1950.*]