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UNITED STATES PATENT OFFICE.

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ADHESIVE OR BINDER.

No Drawing. Original application filed March 4, 1922, Serial No. 541,249. Divided and this application filed October 24, 1923. Serial No. 670,541.

To all whom it may concern:

Be it known that I, FRANCIS G. OKIE, a citizen of the United States, and a resident of St. Paul, Ramsey County, Minnesota, have invented certain new and useful Improvements in Adhesives or Binders, of which the following is a specification.

My present invention relates in general to the treatment of material, preferably in sheet form, and more particularly the treatment of material for the purpose of forming or attaining composite structures, of which well known forms of abrasives such as what is commonly known as sand-paper is an example.

The present application is in part a continuation of my prior application Serial No. 428,287, filed December 4, 1920, and a division of my prior application Serial No. 541,249, filed March 4, 1922.

Although I hereinafter disclose the practice of my invention in connection with abrasives such as sand-paper, it will be understood that my invention, or certain features thereof, have a wider field of utility.

Composite structures of the abrasive type such as sand-paper or emery cloth comprise generally (*a*) a base of sheet material, which may be felted as in the case of paper or woven as in the case of cloth, (*b*) a more or less finely comminuted resistant material having abrading properties, such as garnet or corundum, and (*c*) a binder generally in the form of a glue which serves to bind the abrasive to the base.

The abrasive products as produced at present have as incidents certain features among which are affinity for moisture, rendering them substantially inutile in the presence of water or moisture, and cracking, with consequent exposure of the base, when bent.

The principal objects of my present invention are the provision of a binder which functions more efficiently than any known to me; the provision of a binder characterized by flexibility without cracking or other undesirable effect; the provision of a binder characterized by extensibility and compressibility to accommodate itself to flexion of the base; the provision of a binder by means of which the desired adhesive action between it and the base is attained not only efficiently but also with a desirable degree of acceleration, and more particularly the provision of a binder in which the drying action will be effective from the contact surface between it and the base outwardly; the provision of a binder in which the drying action will be effective from the outer surface inwardly; the provision of a binder characterized by a drying action that permits of handling the product with a minimum of delay and more particularly such handling without impairment of the superficies of the material; the provision of a binder characterized by a limitation of its drying action; the provision of an improved moisture-proofing treatment for material, and especially material in a sheet form, and more particularly for causing a moisture proofing agent to penetrate into the material to an extent short of exudation on an adjacent surface thereof; the provision of a moisture-proof composite abrasive structure; the provision in such an article of a binder having moisture-proofing functions, and the provision generally of an improved flexible waterproof composite abrasive structure, together with such other objects and additional benefits and advantages as may hereinafter appear or be pointed out.

In the employment of my present invention for the production of sand-paper and the like (which I cite for purposes of example) I use as the base such a sheet of material (which may be paper) as will conveniently serve the employment contemplated, and as the abrasive such comminuted material (which may be crushed garnet) similarly adapted to serve the function in view.

It is desirable that the binder utilized have the functions and characteristics not only of great mechanical strength and of great binding strength, but also that it be non-hygroscopic, permeative, moisture-resistant, easily worked, readily obtainable, inexpensive and facilely applied.

I have discovered that gums or resins of such types as are used in the manufacture of the better grades of varnish are peculiarly adapted for the attainment of these ends and that gums or resins such as kauri, copal, dammar are examples of these types. Gum dammar is preferred by me as best attaining the desired ends, viewed from certain aspects.

In preparing the binder for use, the gum or resin is used in connection with a suitable vehicle which I prefer is of a type such as linseed oil or china wood oil, for reason which I will proceed to explain.

In applying a gum or resin prepared with a vehicle such as linseed oil to one surface of a base of paper for example I have found that the action of the vehicle involves a penetration of the base by the vehicle, for example linseed oil, to a point which approximates the opposite surface of the sheet but falls short of actual exudation of the vehicle upon such opposite surface. This results in a moisture-proofing of the material against the destructive absorption of moisture through the surface opposite to that to which the binder is applied, without at the same time defacing or otherwise undesirably affecting such opposite surface.

This penetration by the vehicle, particularly when coupled with the use of the character of gum or resin pointed out above, carries with it in such penetration a certain amount of finely divided gum or resin so that a coating and binding action is secured between the fibres or elemental portions of the base which thus substantially retards, if it does not entirely prevent, disintegration of the material of the base, in addition to preventing access of moisture through the base to the plane of contact between the base and the main mass of the binder material.

The efficient action of the binder may be enhanced in the manufacture of sand-paper if the binder is applied to the base by the use of pressure and the more or less finely divided abrasive is then applied in such a manner as to cause it to adhere to the binder.

In order to accelerate the adhesion between the binder and the base, I have discovered it desirable to use with the binder a modifying agent the action of which is to cause a desiccation of the binder initiated at the contact surface of the binder with the base and effective outwardly.

In my experience I have discovered that there are a number of materials having a metallic base which are useful for my present purposes, that manganic oxides are peculiarly useful and that borate of manganese best combinates siccative energy with the desirable susceptibility to fine grinding.

Due to the relatively slow drying of binders generally difficulties are encountered in handling the structure, within a convenient period because of the soft and sticky character particularly of the exposed surfaces of the binder. This objection I mitigate by associating with the improved binder a substance the action of which is to produce an accelerated drying action effective primarily at the exposed surface and working inwardly, and for this purpose I incorporate in the binder a modifying element peculiarly effective in its action as an oxidizing agent on such vehicles as linseed oil and as a penetration retarding agent with reference to the excess absorption of the vehicle by the base.

The substance I have discovered to be particularly adapted for this purpose is that carbonate of lead or white lead well known to the trade, obtainable in the open market and formed by a new electrolytic process and which in my experience is found to be more satisfactory than any other known form of carbonate of lead.

Whereas by itself the white lead adds but relatively little strength to the binder, in association in the binder with the borate of manganese it intensifies the action of the binder in holding the abrasive firmly against the base.

For intensifying the binding action of the binder and for intensifying the drying action of the dryers, and at the same time accomplishing such ends by the employment of a material which is efficacious in holding the mineral elements in suspension without loss of siccative energy or reducing the relative fluidity of the material, I have discovered that it is advantageous to employ as part of the binder a paste dryer. This may comprise such substances as sugar of lead and borate of manganese suspended in a resinous vehicle but I find it preferable to form the paste dryer so as to have the substances contained therein in the form of sub-acetate of lead and resinate of manganese. I have found by experience that the paste dryer should be somewhat in the nature of cheesy butter, rather softer, and of a light brownish grey color.

As an auxiliary in (1) accentuating the adhesion of the binder to the paper, (2) facilitating to a certain extent the spreading of the binder, and (3) modifying as desired the consistency of the binder as is useful in cases where it is desired to render it more fluid, I have discovered that the use of a japan dryer is desirable. Such a dryer characterized by relative freedom from rosin, is preferable. One form of this contains shellac, red lead, litharge, manganese oxid, burnt umber, gum, linseed oil and turpentine q. s.

In order to give the binder the desired bulk I preferably employ a varnish consisting largely of an oil which may be hardened such as linseed oil boiled until it reaches nearly a solid state. As far as feasible this should be as free as possible from glycerides and fatty acids.

The aforementioned gums or resins, such as gum dammar are preferably employed in the form of a varnish which is substantially three parts Batavia dammar, with two parts kettle boiled linseed oil.

While gum copal and gum kauri in cer-

tain respects make more substantial binders than gum dammar, as they will carry more oil and dry harder under certain conditions as may be useful for certain purposes, generally speaking the present relatively greater expense does not ordinarily justify their use for most purposes, which are well served by gum dammar.

Though I have hereinabove disclosed certain forms of useful dryers having various characteristics, and likewise intensifiers, I have discovered that where it is advisable that the siccative action thereof be limited, or at least retarded, under certain conditions, or when producing material for certain purposes, that it is desirable to incorporate in the binder a non-drying oil such as castor oil or the like, for such purpose.

Sand-paper made in accordance with the disclosure of my present invention is characterized by great flexibility without any adverse effects, such as cracking of the binder or base, or loosening of one from the other; and great resistance to water, and moisture generally, and is highly resistant to deterioration in the presence of friction and moisture when used in a water-abrading operation.

The materials used by me as hereinabove described may be varied in character so as to vary the characteristics of the binder from the stand-point of adhesiveness, non-hygroscopy, and flexibility. Where such variations in the use of materials is employed to produce, for instance, increased adhesion between the binder and the abrasive, such increase may be attained, though possibly at a certain expense of its characteristic of flexibility.

Due, however, to this very same increased adhesiveness, one or more of the outer layers of the base may be removed as by the employment of a base which involves the use of a built up structure having a number of plies, certain of which may be removed, or by shaving off part of the thickness of the base.

By this process I am enabled to obtain sand-paper characterized by extraordinary thinness and flexibility, in that I am able to form sand-paper and the like with a base so thin that such product could not be manufactured, if the base originally used were of the thinness ultimately desired.

In my preferred practice, I form batches which by weight and percentage contain the following ingredients:

		Pounds.	Per cent.
Part I.	Carbonate of lead	24	.1666
	Gum varnish	6	.0416
Part II.	Borate of manganese	6	.0416
	Gum varnish	6	.0416
Part III.	Dryer	6	.0416
	Paste dryer	6	.0416
	Linseed oil varnish	48	.3333
	Gum varnish	42	.2916

This gives a composition of matter wherein metallic and resinous bases are combined in the proportions of substantially one to three; for instance, from above formula:

			Parts.
Gum varnish	6	White lead	24
Gum varnish	6	Borate of manganese	6
Gum varnish	42	Dryer	6
Linseed oil varnish	48		
Dryer	6		36
	108		

The foregoing assumes that 6 parts of each of the japan and paste dryers are divided to the metallic and resinous bases.

In such preferred practice, Parts I and II are mixed and milled separately since Part I mills more readily than Part II, and are desirably then mixed with Part III and the composite batch is then milled until smooth.

Parts I and II include the gum varnish in order to attain not only a fine subdivision of the metallic substance but also to render them readily commiscible with Part III.

In the preferred practice of my invention, in forming Part I hereinabove referred to, I grind the carbonate of lead and the varnish to an exceeding fineness which may be accomplished by passing them through a fine-grinding mill three or four trips. The material grinds quickly and easily and may be conveniently mixed in the mill. One of the functions of the carbonate of lead is to hasten the oxidization of the thinner (and greasier) elements of the binder and limit their absorption by the base, e. g., paper in the case of sand-paper. It also hastens or accelerates the superficial top-drying of the sand-paper or the like, rendering it among other things easier to handle before it becomes dry. Ordinary white leads, even though of apparent equal purity and of similar analyses as that herein referred to, do not function as satisfactorily for chemical reasons not yet brought to light by my experience.

Gum varnish may be No. 1 gum kauri, gum copal, or gum dammar or more or less numerous similar suitable gums or resins melted in boiled or raw linseed oil, with or without the presence of dryers, such as red lead, litharge, black oxid of manganese, burnt umber, and the like. The gum varnish preferably used by me in Parts I, II and III above referred to, is substantially equal parts Batavia dammer gum, and kettle boiled linseed oil. While I preferably use gum dammar, as just indicated, I have found a gum dammar varnish made from three parts Batavia dammar, melted by itself under gentle heat, as is preferable

though it may be used cold, and two parts of a hydrocarbon (which may be one of the petroleum series), obviously added after the heat, if used, is discontinued. The hydrocarbon referred to preferably takes the following form:

Color, water white; Baumé, 48–49°; initial boiling point not below 275° F.; not more than 50% over at 340° F.; recovery, at least 95% residue, colorless; end point, below 475° F.

As the hydrocarbon evaporates, it may be advisable to add more to the mixture in order to preserve the desired degree of fluidity. The hydrocarbon dammar varnish thus formed makes a more brittle binder than the linseed oil gum dammar varnish above described. Although gum copal and gum kauri each make a more substantial binder than gum dammar, as they carry more oil and dry harder, they are more expensive, gum dammar not oxidizing to such a degree of hardness and toughness is more highly flexible, but within my experience comprises as great a step towards common rosin as at present advised it appears expedient to take.

I have found that synthetic gums or resins can also be used to good advantage in making a binder for my purposes.

In using borate of maganese I have found that a well-known borate of manganese, readily obtainable on the open market combines best siccative energy with susceptibility to fine grinding and to form Part II referred to above it should be ground in the varnish until it may be spread on a glass without being mealy under one's finger. It should be ground until experience shows that it can be ground no finer.

As will be appreciated from the foregoing discussion, the siccative energy of the borate of manganese operates from within outwardly, differing in this respect from the carbonate of lead which oxidizes from without inwardly.

While I prefer to employ manganic derivatives in the form of borate of manganese, it is to be observed that although black oxide of manganese contains certain desirable siccative elements for my purposes, it does not readily lend itself to grinding in such a manner as is desired by me. At times, advantage may be taken of the characteristics of black oxide of manganese by heating it in linseed oil.

Similarly, cobalt derivatives, (such as acetate of cobalt) may be employed for their siccative qualities, but I have found that due care should be employed in using such highly concentrated dryers so as to avoid any tendency toward deterioration and relative inactivity with the other dryers; failing such care such cobalt derivatives do not give such excellent effects as borate of manganese.

In forming Part II according to my preferred practice, I find it desirable to grind the borate of manganese by itself, ten or twelve trips if necessary, as this is relatively a very hard substance to grind, and the varnish may be mixed therewith in the mill.

The form of japan-dryer preferably employed by me is a well known japan which contains about 2% (two percentum) of shellac, preferably the best obtainable, besides substances such as red lead (Pb_3O_4) litharge (PbO) manganese oxid (MnO) burnt umber (which has a manganic and oxygen content) and gums in linseed oil and turpentine. It aids in the binding action and acts to some extent as a thinner whose turpentine content evaporates after the binder is spread on the paper and somewhat facilitates the spreading process. I have the proportion indicated in Part III as ordinarily adequate but yet capable of increase with safety when larger quantities are desirable. Although to an unaccustomed observer a rosin content in the japan may, due to its rapidity of action, appear to be advantageous, such a content is within my experience undesirable, and to be avoided.

To form the linseed oil varnish of Part III above referred to, linseed oil is boiled until nearly solid. A heavier grade than ordinary, having less glyceride and fatty acid content than is usual, although a bit more difficult to handle, has been found by me in actual practice to be slightly better in its functions.

In preparing the paste-dryer of Part III above referred to, I first form the initial portion of the dryer by stirring 200 pounds of litharge (PbO) and 200 pounds of hot water (120° F), the agitation of the water being sufficiently violent during and after the addition of the litharge to keep it from settling. After, say two to five minutes of this sustained agitation, 45 pounds of 80% acetic acid is dashed into the hot-water and litharge composition without cessation of the violent stirring, which may be mechanical agitation, and which should continue until the milky white liquid that develops as soon as the acid strikes the water and litharge, sets to a consistency resembling soft cottage cheese or bonny clabber and offer resistance enough to tend to slow up a strong man using a paddle.

In cases where a mechanical agitator is used, it should be shut off at this stage which is ordinarily reached within a minute after the acetic acid is dashed in. It is advisable to have the agitation sufficiently violent to cause suspension of all of the litharge and to dash in the acetic acid suddenly, as otherwise a quantity of uncombined litharge will be found at the bottom of the mixer, and the mass, which is now basic acetate of lead,

will not set stiff. This resultant mass should be undisturbed for about 15 hours and then 75 pounds kettle boiled linseed oil is added to the mass, which by this time has become somewhat stiffer. The whole mass is then mixed preferably in a mechanical mixer. The mixer should be run until a large percentage of the original water may be poured off. At this time the basic acetate of lead has a greater affinity for the oil than for the water. When further agitation separates out no more water, the compound should be ground. This may be done on 3 roller ink mill until no more water can be discerned, and when substantially all of it can be accounted for by weighing the water that has been poured off. The strength of the acetic acid may be varied below 80% provided the proportions are changed correspondingly to the strength of the acetic acid.

While the second part of the paste dryer may be formed by heating, I prefer to mix thoroughly 100 pounds of kettle boiled linseed oil, with 75 pounds of resinate of manganese (powdered form) and then grind the mixture two or three trips until fine and smooth.

I then add 225 pounds kettle boiled linseed oil to the lead compound formed in the mixer as above set forth, and then quickly mix the resulting mass of the second portion with the modified first or lead compound portion which is in the mixer as just set forth.

This mixing of the two portions should be done quickly because there is a nicely balanced proportion between the two, and an excess of either portion in long contact with the other portion, imperfectly mixed, causes a livering and sometimes a separation therebetween. After this mixture of the two portions has stood for substantially an hour, they should be milled one trip. This completes the paste dryer.

It should flow down the apron of the mill about one inch deep, (more or less, depending partly on tightness of rollers and consequent heat,) and it should be kept in stock in a consistency about like cheesy butter, but rather softer, and of a light brownish gray color.

By having the manganic derivative precipitated or combined with a more substantial gum than rosin (resinate of manganese) in the formation of this paste dryer results are attainable which from certain aspects present obvious advantages.

From the foregoing description it will be apparent that one of the general functions of the carbonate of lead is to serve as filler, and of the borate of manganese, as well as of the japan composition referred to, is to serve as a dryer, and that the rest of my improved binder is made up of varnishes.

The gross formula of the binder considered from this aspect of the invention, therefore involves the use, generally, of four parts "filler," three parts "dryer," and seventeen parts "varnish," preferably associated together in the specific manner set forth.

The binder is formed, in my preferred practice, by running together through the mill parts I and II, ground finely as described, together with the items of part III, all three parts being milled together until the whole mass is uniform and smooth. The binder thus formed should be kept carefully covered preferably in contact with oiled paper to prevent the formation of surface skin through exposure.

Having thus described my invention and illustrated its use, what I claim as new and desire to secure by Letters Patent is:

1. A waterproof adhesive including a mixture of substantially three parts drier materials, four parts white lead, and seventeen parts varnish material combined to render such adhesive stable and resistant to deterioration in the presence of friction and moisture when used in a water-abrading operation.

2. A waterproof binder for attaching grit to a surface for forming base to form waterproof sandpaper, for employment in a water abrading process, which includes a mixture of varnish, drier and filler materials affording an inert binder for attaching the grit to the base and resisting rapid deterioration of such binder when employed in a water abrading operation.

3. A waterproof binder for sandpaper which is characterized by flexibility when solidified, substantial inertness, and possessing tenacity and durability sufficient to substantially resist rapid deterioration in the presence of friction and moisture when employed in a water abrading process, said binder including varnish, drier and filler materials and having the dual properties of affording a tenacious retaining means for the grit and to permeate the base for rendering the latter waterproof.

4. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive including an oil which when hardened is of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry.

5. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive including a gum which is of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained ap-

plication of or immersion in water, said adhesive being flexible when dry.

6. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive including a resin which is of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry.

7. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive including a gum varnish which is of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry.

8. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive including the combination of an oil and a resin which combination is of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry.

9. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including a base material which is flexible and waterproof and a penetration retarding agent.

10. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including a base material which is flexible and waterproof and a desiccating agent.

11. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including a base material which is flexible and waterproof and a desiccation retarding agent.

12. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including a base material which is flexible and waterproof, penetration retarding agent and a desiccating agent.

13. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including a base material which is flexible and waterproof, a desiccating agent and a desiccation retarding agent.

14. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including as a base material which is flexible and waterproof, the combination of a desiccating agent which accelerates the drying of the adhesive from the surface which is in contact with the air.

15. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including as a base material which is flexible and waterproof, the combination of a desiccating agent which accelerates the drying of adhesive from the surface which is out of contact with air and in contact with the article to which the adhesive is applied.

16. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including as a base material which is flexible and waterproof, the combination of a plurality of desiccating agents one of which accelerates the drying of the adhesive from the surface which is in contact with the air, and another of which accelerates the drying of the adhesive from

the surface which is out of contact with air and in contact with the article to which the adhesive is applied.

17. A waterproof adhesive bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water said adhesive being flexible when dry and including as a base material which is flexible and waterproof, the combination of a desiccating agent which accelerates the drying of adhesive from the surface which is out of contact with air and in contact with the article to which the adhesive is applied, and a penetration retarding agent.

18. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry and including a base material which is flexible and waterproof, and white lead.

19. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry and including a base material which is flexible and waterproof and castor oil.

20. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry and including a base material which is flexible and water proof and borate of manganese.

21. A waterproof adhesive for bonding grit to a surface forming base to form with such base an article in the nature of flexible waterproof sandpaper, said adhesive being of a nature to maintain its bonding effect when said adhesive is subjected to friction even under sustained application of or immersion in water, said adhesive being flexible when dry and including a base material which is flexible and waterproof and a japan dryer.

In testimony whereof I have hereunto signed my name.

FRANCIS G. OKIE.