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BINDER FOR AGGLOMERATING FINELY DIVIDED MATERIALS

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This invention relates to binders for agglomerating finely divided materials preparatory to heat treatment, and has for its object the provision of an improved binder for such purposes and a method of making the same. More particularly, the invention contemplates an improved binder and method of making the same for incorporation in a finely divided pre-fired mixture of metal oxides preparatory to pressing the mixture into shaped articles for final-firing in accordance with the invention of my United States Letters Patent 2,575,099, patented November 13, 1951.

Patent 2,575,099 describes a method of making magnetic compositions in which a metal oxide mixture containing 50 to 90% by weight of ferric oxide and two or more other metal oxides is subjected to multi-stage heat-treatment (including pre-firing and final-firing) at temperatures within the range of 800 to 1500° C. The pre-fired product after fine grinding (usually to a particle size mostly between 1 and 20 microns), is compacted and pressed into shaped articles (e. g. magnetic cores) with the aid of an appropriate binder; and the shaped articles are subjected to final-firing. The environments in which heat-treatment is carried out are so controlled that ferrous oxide is present in the product resulting at the conclusion of final-firing, and that product is gradually cooled through at least the greater part of the temperature range in which ferrous oxide spontaneously dissociates into metallic iron and magnetite. Preferably, the binder incorporated in the pre-fired product is a carbonaceous material capable of additionally serving as a reducing agent during final-firing. Compacting and pressing of the pre-fired product and added binder into shaped articles is carried out in any suitable apparatus under a pressure of at least 5000 pounds and more usually between 20,000 and 40,000 pounds per square inch.

I have found that a satisfactory binder for the aforementioned purpose should serve several functions, namely (1) impart sufficient moist plasticity to the finely divided material to insure intimate mixing of the binder therewith, (2) impart a lubricating quality during pressing of the shaped articles, (3) impart adequate green strength to the shaped articles for subsequent handling and transfer to the final-firing kiln or furnace, and (4) provide the desired amount of carbonaceous reducing agent during final-firing. No single substance appears capable of performing these necessary functions, and the present invention is the result of an exhaustive investigation in the endeavor to compound a satisfactory complete binder from several compatible components.

The binder of the invention, in its complete form as mixed with the finely divided or powdery material to be agglomerated, e. g. pressed into shaped articles, is an aqueous mixture of three essential components which may be generally classified as (1) a wax-like lubricant, (2) a resin capable of providing residual carbon upon heating, and (3) a compatible resin plasticizer. The aqueous component of the complete resin serves as the vehicle in which the other components are uniformly dissolved or dispersed, and provides the water required for uniformly incorporating the binder throughout the entire body of the finely divided material to give a resultant moist, plastic mass. The amount of water required for imparting this initial moist plasticity is generally of the order of 10% on the dry weight of the finely divided material with which the complete binder is to be mixed. Since practically all of this water is removed during drying of the mixture of material and binder preparatory to pressing, the water is not functionally a component of the actual binder.

The wax-like lubricating component of the binder is preferably a salt or ester of stearic acid, such as calcium stearate, zinc stearate, butyl stearate etc. In lieu of a stearate, stearic acid may be saponified in situ, during the preparation of the binder, by reaction with any appropriate saponifying agent such as triethanolamine. Calculated on a dry basis, the amount of lubricant exceeds the combined amount of resins in the complete binder, and in general for each 10 parts by weight of lubricant the complete binder contains 4 to 8 parts by weight of combined resins, all on a dry basis. Similarly on a dry basis, the complete binder contains 10 to 20 parts by weight of resin plasticizer.

I have found that the resin component of the binder should be in part water-insoluble and in part water-soluble. While the explanation for the advantages of such a two-part resin component is presently somewhat obscure, it is believed to be due (in some measure at least) to the fact that the solvents (acetone, alcohol etc.) for water-insoluble resins volatilize too rapidly and leave the resin-impregnated powder in too hard a physical condition for pressing. On the other hand, where a water-soluble resin is used solely, the time required to remove the solvent, i. e. water, intimately associated with the resin is inordinately long and objectionably slows down the manufacturing operation. Accordingly, the resin component of the binder is made up of about 2 parts by weight of a water-insoluble resin, preferably of the phenol-formaldehyde type, and about 1 part by weight of a water-soluble resin, preferably of the incompletely condensed urea-formaldehyde type.

Any suitable resin plasticizer may be included in the binder. As examples of such plasticizers may be mentioned tricresyl phosphate, dibutyl sebacate, o-cresyl p-toluene sulfonate, and Carbowaxes which are polyethylene glycols marketed by Carbide and Carbon Chemical Company. When stearic acid is saponified with triethanolamine, the latter also serves in some measure as a plasticizer. Carbowax has been found peculiarly advantageous in the binder of the invention since it acts as an inhibitor of polymerization of the resins during the operations of mixing the binder with the finely divided material and subsequent low temperature drying. Polymerization of the resins results in a hard mixture which is difficult to press and additionally exerts a deleterious effect on the electrical and magnetic properties of the finished shaped articles.

The binder is conveniently prepared by melting the wax-like lubricant, usually at a temperature not exceeding and usually somewhat under 200° F., and while maintained in the melted state at about that temperature mixing the plasticizer therewith. During cooling of the resulting product, sufficient water is added so that when the complete binder is subsequently mixed with the finely divided material a moist, plastic mass is obtained. Generally, the amount of water so added is about 10% on the weight of the material with which the complete binder is to be mixed. The resins are added to the cooled mixture of lubricant, plasticizer and water. The resins are preferably added in liquid form, as an aqueous solution of the water-soluble resin and dissolved in an organic

solvent such as an alcohol, a ketone like acetone etc., in the case of the water-insoluble resin. The aforementioned constituent components of the binder may, by way of example, be 10 parts by weight (on a dry basis) of calcium stearate, 15 parts of Carbowax, and 4 to 8 parts of combined resins in the relative proportions of 2 parts of water-insoluble resin and 1 part of water-soluble resin.

About 2 pounds (on a dry basis) of the complete binder is mixed with each 100 pounds of the finely divided material, mixing being conveniently carried out in a dough-type mixer. The resulting mixture is dried to eliminate water. Drying may advantageously be carried out in the mixer or in an oven at a temperature of about 220° F. The dried mixture is easily granulated and flows readily into the press cavities, where it is pressed under a considerable pressure into shaped articles. The fluidity of the mixture needed for pressing is maintained since none of the binder's components, i. e. lubricant, resins and plasticizer, volatilizes at the drying temperature. In the course of final-firing, the non-resinous components of the binder volatilize easily and rapidly within the temperature range of 400 to 600° F. At temperatures above about 500° F. the resinous component of the binder decomposes leaving residual carbon uniformly dispersed throughout the mass of the shaped articles undergoing final-firing. The resinous component of the binder imparts green strength to the shaped articles, both as pressed and while heating up to relatively low temperatures, and also supplies the carbonaceous reducing agent contemplated during final-firing in the method of Patent 2,575,099. The carbonaceous residue should be kept to the required minimum, since more than required for the contemplated reduction is difficult to burn out. Hence, the amount of resin (on a dry basis) mixed (in the form of the complete binder) with the finely divided material is about 0.25% to about 0.5% by weight.

When the wax-like lubricant is formed in situ by saponification of stearic acid, a mixture of 6 parts by weight of stearic acid and 4 parts of triethanolamine is heated to approximately 190° F. until a clear melted liquid (straw-colored) is obtained, and while maintained at 190° F. 15 parts by weight of tricresyl phosphate (or equivalent plasticizer) is added thereto. During cooling of the resulting wax-like reaction product, water (in the amount previously mentioned) is added thereto. From 4 to 8 parts by weight (calculated on a dry basis) of combined water-insoluble and water-soluble resins (in the relative proportions of 2 parts and 1 part, respectively) are added to the cooled aqueous mixture to complete the binder.

I claim:

1. A binder for agglomerating finely divided metal oxides preparatory to heat-treatment at a temperature within the range of 800°–1500° C. containing as essential components stearic acid in saponified form, an alcohol-soluble, water-insoluble phenol-formaldehyde resin, a water-soluble, partially condensed urea-formaldehyde resin, a compatible plasticizer for the resins, the relative proportions of saponified stearic acid, resins and plasticizer, calculated by weight on the dry basis, being 10 parts, 4 to 8 parts and 10 to 20 parts, respectively, and about 10% of water on the dry weight of said components.

2. A binder according to claim 1 in which the relative proportions of the phenol-formaldehyde resin and the urea-formaldehyde resin, calculated by weight on the dry basis, are 2 parts and 1 part, respectively.

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