UNITED STATES PATENT OFFICE.

CLEMENS DÖRR, OF GERMERSHEIM, GERMANY.

PRODUCTION OF SOLID MATERIALS FROM TAR, &c.

SPECIFICATION forming part of Letters Patent No. 691,934, dated January 28, 1902.

Application filed July 20, 1899. Serial No. 724,557. (No specimens.)

To all whom it may concern:

Be it known that I, CLEMENS DÖRR, a subject of the German Emperor, and a resident of Germersheim, in the Empire of Germany, have invented certain new and useful Improvements in the Production of Solid Materials from Tar and other Substances, of which the following is a specification.

The present invention relates to the production of solid materials having varying hardness from that of hard wood up to that of granite by means of a hitherto unknown capacity of tar to form a solid binding material when it is combined in the particular manner hereinafter described with a certain proportionately-large excess of various filling materials.

The use of tar with or without the addition of resin and filling materials for the covering of roofs and the like, which mixture hardens under the action of the air, is well known; but the use of the filling material in an excess for this purpose is limited by the necessity that the mixture should be somewhat fluid when it is applied. It is also known that the pitch-like residue from tar distillation, with or without the addition of bitumen and mixture of chalk, gravel, or other finely-divided material, can be used as an artificial asphalt for paving and the like or can be cast in molds, so as to form blocks of various shapes. In this case the binding material in its heated condition is already somewhat fluid and must be sufficiently so in order that after the addition of the sand, gravel, or the like it may still be fluid enough to be poured into molds or otherwise poured onto the place where it is to be used. Pitch only contains the heavy oils of tar, while the light oils and the medium oils have been driven off by distillation. The present invention differs from both these methods not only in the process, but also in its products. It is based on the following observations: When tar is heated, there are first formed whitish vapors. As the heating is increased these vapors turn to grayish-blue, then to yellow, and then into a more intense yellow with weak grayish tinges, and lastly again to a grayish color. If this heating process is interrupted at any time during these various stages and the remaining mass is tested after the loss of the distillation products which have passed off in the aforesaid vapors, there will not be found any appreciable difference between this mass and the original tar. It is sticky to the finger, comes off to the touch, and does not become solid. It is, indeed, altered in its chemical constitution; but externally the alteration is not easily visible. If the same process is carried out with a mixture of tar and solid granular or otherwise finely-divided inorganic or organic bodies—for example, sand or sawdust, or a mixture of these materials, these materials being in excess in proportion of at least three to one in volume—the vapors given off from the tar will have the same appearance and pass off in the same sequence, and should the process be interrupted at the various stages it will be found that at a certain period of the process a remarkable change in its constitution takes place. Thus the mass will at first before it is heated appear simply a mixture of a somewhat thick tar with the filling materials and will have more or less the qualities of ordinary tar—such as stickiness, &c.—and when the mass is heated it will still for some time show the properties of a thickened tar; but at a certain period this appearance will alter—namely, when the temperature of the mixture has remained for some time between 160° and 190° centigrade—that is to say, also when the yellow vapors have ceased and the grayish vapors have commenced to pass off. If the operation is interrupted at this stage, the mass will no longer appear as a fluid or even as a viscid material, but will appear dry and of the consistency of mortar or cement. It no longer comes off to the touch nor attaches itself to the finger; but if pressed now between the fingers it will be found to be plastic. It is no longer fluid enough to be poured, as would be the mixture of pitch or asphalt with filling materials; but it can be made into forms by placing it in molds and pressing or stamping it. When these are cold, the material becomes a solid body, which, according to the nature of the filling materials used in its appearance and qualities, approaches more or less to a natural stone and no longer shows in any way the particular qualities of a tarry mixture. In order to produce such a product, it is important to interrupt the heating process when the tem-

perature is between 160° and 190° centigrade. The yellow vapors must have passed into gray. This is the period at which the process of heating of the mass is complete. If the process were carried further and, for example, interrupted when the temperature of the mass had for some time exceeded 200° centigrade, or if for some time gray vapors have been passing off, the mass will be overheated, and the product will no longer be a coherent solid of the necessary nature, but will be a friable mass, which will be technically worthless. If, on the other hand, the complete process of heating of the mass is not reached, but the process is interrupted too early—for example, below 150° centigrade—the product when completely cold will be still soft and remain unsuitable for the purpose for which it is intended to be used. The most suitable temperature is between 160° and 190° centigrade; but the temperature and the duration of the process might be extended so far that the temperature exceeds 200° centigrade for a short time without being hurtful to the product.

The chemical and mechanical aspects of the process are as follows: During the heating the ammonia-water and the most volatile of the oils contained in the tar, especially benzol and toluol, are first given off in the form of vapor as the temperature rises. The less volatile of the light oils (xylol and its higher homologues, such as phenol) are given off, the boiling-point of which is below the temperature in the retort. The oil-vapors naturally take with them a small amount of the more heavy bodies from the tar, specially naphthalene and small quantities of the higher phenols (cresol) and hydrocarbons. On the other hand, the hot tar will still contain small quantities of the above-mentioned lighter oils, whose boiling-point is not very far below the temperature of the retort. These small quantities are technically insignificant and do not affect the result of the process. It is important on the whole that water and the more volatile oils should be evaporated, while medium oils, also those which by heating above the given temperature would be evaporated, should be retained in the mixture. After the distillation is completed according to this process the tar will have lost in all from seven to ten per cent. of its quantity. The particles of the filling materials become coated with a thin layer of the binding material, and by means of pressure they are firmly cemented together. The binding material becomes solid in the cold and forms an insoluble cement for the particles of the filling materials. If the medium oils are absent, as in previous processes, this binding of the larger quantities of filling materials which are present in this process will not take place.

In the practical working out of this process an open fire is not used for the heating, as thereby a partial superheating of the mass would take place; but steam under pressure of a sufficient temperature is used for the heating. During the process of heating the mass must be kept moving. The completion of the process—that is to say, the completion of the heat action desired—is indicated by observing the color of the vapors, or it may be found by taking a sample and seeing that it has the desired properties. If the desired period is passed, even only for a few minutes, the result will be that the product will quickly pass into that state in which it is completely useless. When the heating process ceases, the material still in the hot state is placed in suitable molds and pressed or stamped, so as to condense it therein. It can then be left to cool naturally or be cooled off by means of water. The finished product in its external appearance does not appear very different whether sand or gravel, on the one hand, or sawdust, on the other, is used as a filling material, nor is there any appreciable difference in appearance, whether more or less of the filling materials are used within the limits of from three to ten parts, by volume, of filling material to one part, by volume, of tar. On the other hand, naturally the structure and physical qualities of the product will offer some variation, according to the amount (within said limits) and nature of the filling materials, and these variations may be utilized in the proportion of the product for various uses. If sharp sand or gravel, the product resembles stone almost of the hardness of granite, and it can be sculptured, cut, or polished in a similar way to marble. If the addition of sand and gravel is very large—for example, such as eight to ten times the amount of the tar—this stone-like material will become pervious to water. The product made with sawdust resembles ebony or vulcanite, and it may be used in place of these materials. By the mixture of the filling materials various products having properties intermediate between those above mentioned will be formed. All these materials are very resistant to acid, and in consequence of their elasticity and structural strength they are very suitable for all kinds of technical purposes.

Instead of using raw tar, tar can be previously prepared before the filling materials are added to it by removing by distillation its watery constituents—that is to say, the tar would be heated to 160° to 190° without the previous addition of the filling material, and then while it is still in a state of heat the binding materials, previously brought to the same temperature, so as not to suddenly cool the prepared tar by which its binding effect would be lost, are mixed therewith. The distillate can be recovered in suitable condensing apparatus.

I am aware that various processes have been proposed and are in use in which tar and filling substances are used to produce an artifi-

cial asphalt; but none of these produce a substance having the hardness of stone such as is produced by my method.

The essential features of my method are the initial use of thin liquid tar and the limitation of the distillation. This combination has not been hitherto used. More particularly with regard to the limitation of the distillation, none of the processes hitherto known show this limitation for the purpose of preventing the distilling away of too much of the thin liquid substances of the tar. In the former part of my specification this feature is expressed in the statement that the so-called "medium oils" must remain in the mixture.

The reason of the great hardness of product is assumed to be the admixture to the tar of large quantities of hard filling substances while the tar is still in a thin liquid state, in which it is capable of receiving and retaining the largest proportion of such filling substances, and that afterward only the most volatile constituents, (the so-called "light oils,") which, together with the ammonia-water, only form from seven to ten per cent. of the raw tar, are distilled away by increasing the heat from 160° to at most 190° under continuous stirring, the operation being discontinued immediately the mass becomes dry to the touch and ceases to give off color. It will then have been sufficiently distilled to leave in the mixture the best binding agent. If distillation were continued, the binding agent would deteriorate and the product would be spoiled.

I therefore claim as my invention—

In the manufacture of artificial stone the process consisting in: adding a quantity of filling material equal to from four to ten times the quantity of tar to liquid tar at a temperature from the normal to 150° centigrade; heating the mixture, under continuous stirring, to a temperature between 160° and 190° centigrade until from seven to ten per cent. of the original raw tar has been distilled away, and the mixture is dry to the touch, and then molding the mixture.

In witness whereof I have signed this specification in the presence of two witnesses.

CLEMENS DÖRR.

Witnesses:

FERDINAND NAUMBURG,

JACOB ADRIAN.