

## UNITED STATES PATENT OFFICE

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PRODUCTION OF USEFUL ARTICLES  
FROM COAL

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This invention consists of improvements in or relating to the production of useful moulded products from coal. It is well known to manufacture a great variety of useful articles by the moulding of artificial resins or plastics. Such articles can be produced in simple pressure moulds or in injection moulds and it is well known that such useful articles are durable, tough and not subject to corrosion. The general object of the present invention is to make similar strong, tough, moulded, useful products from coal.

As is known when bituminous coals having from 13% to 35% volatiles on the dry ash-free basis are heated progressively from atmospheric temperature upwards, there is one part of the temperature range hereinafter called "the critical range" (which varies somewhat for different coals but is always within the limits 300° C. to 500° C.) in which the coal becomes soft. When the coals are heated to a still higher temperature they harden again to form a relatively strong material. At or above the temperature range at which the coal is plastic it undergoes thermal decomposition, volatile matters being driven off. With the majority of these bituminous coals the rate of evolution of these volatile matters may be so rapid as to result in a swelling of the product and the formation of the well-known bubble structure associated with coke. This swelling is herein called "intumescence." Hence in the usual carbonization processes, where the two effects of softening and resetting, and of thermal decomposition with swelling and the formation of cracks operate concurrently, the resulting material is of little or no use for the manufacture of moulded articles of a desired shape, and very little control over the physical characteristics of the material is possible.

The coals which form the strongest cokes are those having between 20 and 30 per cent of volatile matter, which is equivalent to some 80 to 90 per cent of carbon. (Both these values and the swelling number, wherever mentioned in this specification are as determined by B. S. No. 1016.) Such coals usually swell strongly at temperatures somewhat above their softening points and this swelling can set up excessive pressures in ovens, retorts and the like, giving rise to the danger of damage to the walls. To overcome this danger it is a common practice to mix with such coals a proportion of an inert material such as a weakly coking or a non-coking coal or coke breeze and in some cases the coal before carbonization is submitted to an oxidation process at relatively low temperatures. Whilst these methods reduce

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the swelling pressure, the resultant coke retains the typical bubble structure and random fissures.

In other words, as distinguished from the products of this invention, coke has a cellular structure which is clearly visible to the naked eye.

It is common practice in the manufacture of certain articles, e. g. briquettes and carbon electrodes, to add to the powdered carbonaceous starting material a binding agent which is of a tarry or starchy or adhesive nature or molasses (hereinafter called a "binding agent").

In United States specification Serial No. 622,934, now U. S. Patent No. 2,461,365, it is proposed to use a swell-inhibiting agent which is a finely-divided solid material which does not melt within the firing temperature range (namely, a solid pulverulent carbonaceous agent such as pitch coke, non-coking coal or graphite or a solid pulverulent non-carbonaceous agent such as silica or silicates, or silicon or argillaceous material). The presence with the powdered bituminous coal of such finely-divided materials and the other conditions of the said process enable a dense, shrunk product of low porosity to be obtained after firing to a temperature above 550° C. and preferably exceeding 700° C. The agents so used are called "swell-inhibiting agents" on account of their property, when used in the correct proportion and under other suitable conditions, of neutralising the swelling tendency without seriously impairing the agglutinating power of the coal.

The present invention concerns an alternative method of assisting the inhibition of the swelling, distortion and cracking usually associated with the coking of bituminous coal, and includes the steps of admixing with the powdered coal or introducing into the non-oxidising atmosphere in which firing takes place a small proportion of a chemical swell-inhibiting agent.

This invention broadly consists of a method of making moulded products from bituminous coal which method consists in moulding and subsequently firing to a temperature above 550° C. under non-oxidising conditions finely-divided coal having good agglutinating properties in the presence of a chemical swell-inhibiting agent of the type described below, the method being so carried out that the resulting moulded product is not swollen, has a density greater than that of the coal used and has no cellular structure visible to the naked eye.

The expression "swell-inhibiting agent of the type described" includes solid, liquid or gaseous agents which during firing effect a chemical decomposition. Such agents may in the case of

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solids or liquids be intimately mixed with the finely-divided coal or may in the case of gases or vapours per se or produced by volatilization from solids or liquids be brought into intimate and uniform contact with the coal substance during firing (at least during the critical range).

A chemical swell-inhibiting agent includes a substance which during the heating of the article effects a chemical decomposition. Intumescence of the carbonaceous substance is due to the co-existence of solid, liquid and gas phases, the liquid phase being continuous and generating gas which, under certain viscosity conditions, cannot escape without causing swelling. A chemical swell-inhibiting agent may render volatile portions of the coal substance which would otherwise appear in the liquid phase when the coal is softened; a chemical swell-inhibiting agent may itself undergo volatilisation at a comparatively low temperature (even before the softening temperature of the coal has been reached or at the early stages of the softening of the coal) thus providing increased porosity in the moulded article at an early stage in its heat treatment.

In general chemical swell-inhibiting agents may have one or more of the following effects: (1) they may widen the critical firing temperature range by rendering the coal substance more readily decomposable; (2) since the decomposition of the liquid substances produced in the carbonisation of coal is accompanied by the production of solids, the chemical agents may indirectly increase the extent of the solid phase; (3) the escape of gas may be facilitated by volatilisation of the chemical agent itself or by reaction between the chemical agent and the carbon and/or hydrogen of the coal substance so that greater porosity is provided in the moulded article at the earlier stages of its heat treatment. It will be understood that the chemical swell-inhibiting agents may be elements or compounds which are themselves decomposable under heat or which react with carbon and/or hydrogen under heat.

The coal substance is generally recognised to consist mainly of carbon and hydrogen in chemical combination together with small quantities of oxygen and nitrogen chemically combined with the carbon. The chemical swell-inhibiting agents consist of elements or compounds which themselves may decompose or volatilise under heat or which render a proportion of the coal constituents volatile during or below the critical firing temperature range.

The chemical swell-inhibiting agent may be a halogen, a halogen hydride or a halogen compound which generates a halogen or a halogen hydride under the conditions of firing of the moulded article. These agents are herein referred to as "chemical agents of the halogen type."

In the case where the said agent is a solid it can be mixed with the finely-divided coal before moulding. In the case where such agent is a liquid it can be mixed with the finely-divided coal before moulding or it can be applied, for example by spraying, to the moulded article before firing or the liquid may be vaporised and introduced into the firing atmosphere. In the case where such agent is a gas, the gas may be introduced into the atmosphere which surrounds the moulded article during firing.

According to this invention the chemical agent of the halogen type may be used in very small proportions. It is known that the tarry materials which are evolved during the thermal de-

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composition (carbonisation) of coal whether disposed in films on the surface of the solid residue or present as vapours in the interstices, are in part at least unsaturated compounds of high reactivity which play a significant part in both the agglutinating and the swelling effects observed with coking coals. We propose to neutralise or inhibit the swelling effect without serious impairment or even with enhancement of the agglutinating effect, by acting with chemical agents of the halogen type upon these tarry materials and we find the most suitable substances to be those which during the firing process exist as or can generate halogens (Cl, Br, I or F) or halogen hydrides (HCl, HBr, HI or HF). When selecting agents which are halogen compounds, regard should be had to the possibility that the additional elements introduced if present in excessive quantity may oxidise the coal substance or otherwise affect (e. g. in respect of strength or distortion) the properties of the article.

The chemical swell-inhibiting agent may be a member of the sixth group of the periodic system (i. e. sulphur, selenium or tellurium) or a compound thereof which exists as or can generate a volatile hydride in the presence of hydrogen or hydrocarbon at a temperature within the firing temperature range. It will be understood that oxygen and the metallic elements of the sixth group are excluded.

When selecting agents from the compounds of sulphur, selenium or tellurium, regard should be had to the possibility that the additional elements introduced if present in excessive quantity may oxidise the coal substance or otherwise affect (e. g. in respect of strength or distortion) the properties of the article. Examples of such additional elements are oxygen and chlorine.

Thus the agents may be those which during the firing process exist as or yield volatile hydrogen compounds of the sixth group of the periodic table, namely sulphuretted hydrogen ( $H_2S$ ), hydrogen selenide ( $H_2Se$ ) or tellurium hydride ( $H_2Te$ ).

Again the chemical swell-inhibiting agent may be an element of the fifth group of the periodic system or a compound thereof which exists as or can generate a volatile hydride in the presence of hydrogen or hydrocarbon at a temperature within the firing temperature range. It will be understood that the vanadium sub group of the said fifth group is excluded. The agents may be those which during the firing process exist as or yield volatile hydrides of the fifth group of the periodic system, viz. ammonia ( $NH_3$ ), phosphine ( $PH_3$ ), arseniuretted hydrogen or arsine ( $AsH_3$ ), antimonuretted hydrogen or stibine ( $SbH_3$ ) and bismuth hydride ( $BiH_3$ ).

This invention includes a method of making strong, tough, moulded products from bituminous coal without the use of a binding agent which method consists in (1) selecting coal which has good agglutinating properties, (2) selecting a solid or liquid chemical swell-inhibiting agent of the type described, (3) finely dividing the coal and the said agent if solid or ensuring that they are finely divided, (4) intimately mixing the coal and the said agent, (5) moulding the mixture to the desired shape, (6) providing means to prevent oxidation of the moulded article during firing, and (7) firing the moulded article to a temperature above  $550^\circ C$ . and preferably to a temperature above  $700^\circ C$ .

In an alternative form of this invention where the chemical swell-inhibiting agent is not a solid

or a liquid capable of admixture with the finely-subdivided coal, e. g. when the chemical agent is a vapour or gas the above mixing step (4) is omitted and the agent in the form of a gas or vapour is introduced into the non-oxidising atmosphere in which the moulded article is fired.

The various steps of this process will now be described in greater detail.

(1) *Coal*.—The coal selected should be a coal having a swelling number of 2-10 and preferably 6-10 (this swelling number being a more reliable measurer of agglutinating properties than the so-called agglutinating value). Such coal is referred to in this specification as coal having good agglutinating properties. Such coals are obtainable in Great Britain from for example the South Wales, Durham and Kent coal fields. The coals which have been found to be best adapted for use in the present invention are bituminous coals having a volatile matter content which lies between about 13 and 30 per cent and more usually between 22 and 28 per cent calculated on a dry ash-free basis. Their carbon content lies between 80 and 90 per cent, and more usually between 85 and 89 per cent.

In selecting a coal having good agglutinating properties, regard is given to the purpose for which the final product is to be used. Thus where high electric conductivity is required it is desirable to select a coal with a low ash content or where toughness or resistance to rupture is essential the coal selected has preferably a high swelling number.

(2) *Chemical swell-inhibiting agent*.—As above indicated, the chemical swell-inhibiting agent may be solid, liquid or gaseous. In the case of solid agents the material is used in a finely-divided state and it is essential that the agent shall vaporise or shall effect a chemical decomposition during the firing operation. In the case of a liquid agent it is mixed with the finely-divided coal before moulding or sprayed on to the coal before or after moulding or it may be volatilised and introduced into the firing atmosphere.

The proportion of chemical swell-inhibiting agent is quite low; thus it may be from one to five per cent by weight of the coal. The optimum proportion can be readily determined by a simple preliminary test.

(3) *Subdividing*.—The selected coal and agent (if solid) may be ground separately or together in any suitable machine so that more than 95 per cent by weight of the particles pass through a 200 mesh B. S. sieve. In many cases a much finer comminution can be effected with advantage and either the coal or the agent, or both, may be comminuted so that at least 60 per cent by weight of the particles are smaller than 10 microns or so that the specific surface exceeds at least 15,000 sq. cms. per gramme. Both these measurements are as determined by the photo-electric sedimentation method which is described in the "Proceedings of the Conference on the Determination of Particle Size in the Sub-Sieve Range," B. C. U. R. A.—B. C. O. R. A. publication, 1944. Whilst for the strongest products it is necessary that one or the other should be comminuted to the finest state of subdivision mentioned or even finer, the question as to which of the two should be so comminuted, or whether it is necessary that both should be so comminuted, depends on the results obtained in the experimental procedure which is hereinafter described. The grading of the particle sizes when comminuted as described above will generally be such as to secure a satisfactory

degree of close packing, but if desired the coal and/or agent may be further graded as to particle size, in accordance with known principles, to obtain an improved degree of close packing. However, increase in the degree of comminution of the coal may accentuate the tendency towards swelling and where necessary this factor should be taken into account in determining the proportion of swell-inhibiting agent and other conditions of manufacture.

(4) *Mixing*.—The ordinary methods of mixing which are sufficient for example in preparing a blend of coals for carbonisation or briquetting, are inadequate for the process according to the present invention. The strength of the fired product may fall to a half or even less if there is inadequate or faulty mixing. We therefore use a mixing process which can be relied upon to break down any agglomerates and to ensure as far as possible uniform composition of the mixed powders.

It has been found that the strength and other properties of the fired product can be improved or enhanced by passing the mixture through a blending mill of the type solid under the registered trade mark "Kek." This milling step may be repeated with advantage in certain cases and it has been found that with certain mixtures the strength of the fired product is much increased by this more adequate mixing (which is accompanied by a certain amount of further comminution).

The addition of minor properties of other ingredients which have little or no deleterious effects on the product is not excluded.

(5) *Moulding*.—A pressure of the order of 2 tons per square inch is suitable in many cases but with certain mixes and more especially when shaping is effected by extrusion it has been found possible to press as low as  $\frac{1}{2}$  ton per square inch. If complicated shapes are required, pressure up to 6 tons per square inch or higher may be necessary. The optimum moulding pressure for a given mix may also be determined experimentally. For instance, test pieces are made and fired with a standardized procedure except with variations of the pressure applied in moulding. As during the moulding of the article no curing process is involved, the time of moulding may be quite short and it is usually not necessary to maintain the pressure for more than 10 or 15 seconds. The moulding is normally carried out at room temperature, but for certain mixtures it may be desirable to mould at elevated temperatures.

As to the moulding pressure, considerable variation is possible in different cases, but there must always be enough pressure to enable the moulded article to be transferred from the mould to the firing furnace without damage.

The word "moulding" when used in this specification includes extrusion moulding and also includes slip casting or other moulding technique used in the plastics and ceramic industries.

In general the ordinary technique which is used for the moulding of artificial resins and of dry powders is suitable, except that temperatures higher than atmospheric need not be used. Care should be taken to see that the pressure is applied in an entirely uniform and regular manner. Preferably the mould is designed with slightly greater clearance for the plunger than is customary with artificial resins.

(6) *Firing atmosphere*.—The firing, that is to say the heating of the moulded article and the subsequent cooling must be conducted under non-

oxidising conditions. This may conveniently be achieved by packing the article within a protective mass of granular or powdered material which evolves non-oxidising gases or vapours during the firing operation. A suitable material for this purpose is a coal of high volatile content with little or no caking property, such as Warwickshire Brights. A bed of this powdered material is made and is slightly compressed, and the moulded article is then laid in a depression within the bed which has been made, for example by tamping with a solid former of the same shape as the article. If the moulded article is hollow, the interior of the article is filled with the same powdered material. The exposed surface or surfaces of the articles are then covered with the powder, the latter being firmly but gently pressed down.

It is also possible to secure the necessary protection by passing a gas stream through the furnace, for example hydrogen, carbon monoxide, ordinary town gas, or hydrocarbon vapours. In such case the article should be placed on an even support, preferably of fine, loose granular material such as sand or charcoal and care should be taken to see that the gas composition all round the article is as uniform as possible.

Whichever method of protection is employed, and it will of course be understood that any suitable method or combination of methods may be used if desired, it is essential that firing of the moulded article should take place without burning of the surface of the article. This does not necessarily mean the exclusion of all oxygen or other substances which in theory are capable of oxidising carbon, since the vapours evolved during the firing operation may provide adequate protection against small amounts of these substances. If any burning has taken place it can readily be detected, for example by the presence of a thin film of ash and/or by the pitting or cracking of the surface of the article.

As has been stated above, some procedure to prevent oxidation of the article during the carbonization is essential, and also the product obtained can be varied to a considerable extent by the nature of the atmosphere which may be provided. In this connection it should be noted that pressure within the mass is relieved during carbonization partly by the outward diffusion of the volatiles as they are evolved, and partly by the decomposition, under considerable pressure, of hydrocarbons, with deposition of carbon within the interstices of the mass and with production of hydrogen whose rate of diffusion is more rapid than that of the parent hydrocarbons. By this carbon deposition the product is strengthened and made more dense. It is also thought that hydrogen diffusing towards the periphery of the article combines to some extent with liquid or solid hydrocarbons and produces more volatile hydrocarbons which can more readily escape and thus further relieve the internal pressure.

The use of hydrogen as a protective gas may involve a chemical interaction with unsaturated constituents both of the coal substance and of the surrounding atmosphere, and hence the amount of elementary carbon deposited within the interstices of the article may be less than otherwise would be the case, resulting in greater porosity and impaired strength of the product. This effect is reduced to a minimum when the volume flow of hydrogen is as small as is consistent with the maintenance of a non-oxidising atmosphere. The same applies when there are used other pro-

TECTIVE gases or gas mixtures which tend to hydrogenate such unsaturated constituents or to scour them away without the deposition of carbon. If town gas or the like in fact contains an oxidising gas, the latter can be removed by passing the town gas through a heated tube containing charcoal or other readily oxidisable substance.

The use of hydrogen to maintain a non-oxidising atmosphere tends to the production of the black material referred to as M which is also produced when the proportion of swell-inhibiting agent is much in excess of that minimum necessary to inhibit swelling for a given rate of firing.

It would appear that, for the purpose of obtaining good carbon deposition and making a strong product, the non-oxidising atmosphere should consist of or contain an unsaturated hydrocarbon gas or vapour such for example as ethylene or other olefine or other readily cracked hydrocarbons (whether saturated or unsaturated) such as benzene. Whilst such vapours may scour away certain unsaturated constituents evolved from the coal, such constituents will be replaced by another unsaturated substance such as ethylene, which effect would not be obtained when the non-oxidising atmosphere is provided by a gas such as hydrogen or methane.

It is found that an ethylene atmosphere always tends to the production of the alpha component referred to hereafter which is lustrous grey, with a high tensile strength and a conchoidal fracture. This alpha component tends to be produced when the article is carbonized in an atmosphere which comprises the lower temperature decomposition products of coal.

When a coal having a comparatively low volatile content and agglutinating property is used, it is especially desirable to carry out the firing of the moulded article in an atmosphere of a hydrocarbon as above described.

With this process for the treatment either of high or low volatile-content coal, in order to avoid the dilution by volatile matters evolved from the coal of a relatively expensive vapour such as ethylene, it will often be found advantageous to carry out an initial firing operation, for example up to 450° C. in the presence of a cheaper non-oxidising gas such as ordinary town gas, which may with advantage be freed from oxygen and sulphur, and then to submit the fired article with or without cooling, to a further firing operation in the presence of ethylene vapour, for example up to about 850° C. This latter method, in addition to yielding an article which has an especially low porosity, provides for improved control over the process. For example when the non-oxidising means in the first stage is a gas such as hydrogen or ordinary town gas, the hydrogenation and the scouring away of unsaturated constituents both of the coal substance and of the surrounding atmosphere can be tolerated, and hence the volume flow of the gas may be sufficient to remove any danger of burning of the article as the result of the ingress of atmospheric oxygen. Further, the ethylene or other gas or vapour which is used in the second stage will be relatively free from contamination and therefore may be recycled, thus reducing the cost of the process. It will of course be understood that the article must be exposed to these hydrocarbon gases or vapours sufficiently long for the desired amount of deposition to take place, such deposition being accelerated at high temperature. However, at a firing temperature above about

1,000° C. it is probable that the efficiency of the process will be impaired by the deposition of carbon outside the article, for example on the oven walls.

The two stages of firing above described are especially suitable for the treatment of coal of high volatile content. In the case of comparatively weakly-agglutinating coals the shaped articles may lack sufficient strength to withstand a firing operation unless the hydrocarbon gas or vapour is introduced at the outset. And since many of these comparatively weakly-agglutinating coals are also of low volatile content, the deposition of carbon on the inner surfaces of the material or in the voids between them will not be seriously interfered with, nor will it be necessary to use an excessive quantity of gas or vapour.

(7) *Firing*.—The minimum temperature to which it is necessary to fire the articles is in the neighbourhood of 550° C. but in general better results are obtained with a firing temperature in excess of 700° C. It is necessary to ensure that the temperature all round the article is as uniform as possible. The firing schedule may be varied somewhat by the nature of the mix, the degree of comminution, the moulding pressure and the thickness of the article. In general the higher the proportion of volatile-forming constituents in the mixture, the finer the comminution, the higher the moulding pressure and the thicker the article, the slower should be the rate of firing, at least up to about 500° C.

For articles of uniform thickness up to about half an inch, using a mixture in which the volatile content is about 20 per cent, the following schedule will be found suitable in many cases:

Up to 360° C., 1°–2° C. per minute rise  
360–450° C., ½° C. per minute rise  
450–550° C., 1° C. per minute rise  
550–850° C., 3° C. per minute rise

By firing to temperatures higher than 800° C. increased strength and electrical conductivity are obtained, which increase is generally accompanied by further shrinkage of the article. A suitable schedule is the following:

|               | Time           | Degrees C.<br>per minute. |
|---------------|----------------|---------------------------|
| 800–1000° C.  |                | 4                         |
| 1000–1300° C. | at least 1 hr. |                           |
| 1300–1500° C. | at least ½ hr. |                           |

The rate of firing for a particular mixture is best determined by a simple preliminary test. For instance, test pieces are made and fired with a standardized procedure except with variations in the firing rate, and that firing rate which produces the test piece having the desired characteristics, is selected as the firing rate for the production of the moulded articles to be produced from the particular mixture in question. In some cases the optimum strength is obtained by increasing the rate of firing as far as that can be done without incurring the risk of swelling. Even in the range 400–450° C. it is possible with some mixtures to use a rate of one degree per minute.

The whole or a part of the firing operation may be carried out at a pressure above or below atmospheric pressure.

Whilst for the great majority of bituminous coals the foregoing firing schedules and those given in the examples will be a satisfactory guide, it is important to remember that proximate and ultimate analyses of the coal used are not in

themselves a reliable guide to individual behaviour and, more especially, to the extent of the decomposition temperature range in any given coal.

We have found in the manufacture of the moulded products of this invention that strength in the fired products, the other conditions of manufacture being equal, is to a considerable extent dependent on the presence of a component which we have succeeded in identifying in the course of our researches and which we herein call the "alpha component." This can be recognised by the fact that when it is polished, it has an optical reflectance in oil of a relatively high order (exceeding 4.8% on the Seyler scale—Melchett Lecture to the Institute of Fuel, 1942). It is further characterised by high compressive and tensile strength, marked electrical conductivity, and peculiarities in its X-ray diffraction spectrum. The formation of this alpha component which we believe to be a carbonaceous material built up of highly-condensed aromatic rings in the form of plates superimposed on each other with bundles of these plates orientated at random seems to be promoted by ensuring that the reactive substances (which by polymerisation and subsequent decomposition produce the alpha component) are not decomposed by prolonged maintenance within the lower part of the critical range. Hence to obtain the maximum strength, the other conditions of manufacture being equal, it is desirable that the rate of heating should be as rapid as is possible. It will of course be understood that the rate of heating whilst being very rapid must not be so rapid as to cause intumescence.

The building up of the alpha component during the heating operation appears to be a process of polymerization by stages, the creation of the aromatic rings, the plates formed therefrom and the random agglomerates of such plates occurring gradually. If at any stage in this polymerization the rate of temperature rise is too slow, the polymers will decompose and yield hydrogen, methane, etc., leaving as a solid residue a black, amorphous material having an optical reflectance in oil of less than 0.2 per cent which we refer to as the "M-component." The products containing a high proportion of this M component are weak and of restricted use in commerce.

The factors which promote strength in the final product must be correlated with the expedients for reducing swelling and the difficulty appears that most of the factors which promote strength tend in themselves to increase swelling. With a view to obtaining strength, other considerations being left out of account, it is desirable to choose a coal having a naturally high agglutinating power; to comminute the coal to a very high degree of fineness, so that the individual particles can be brought into the closest possible contact; to compress the mass under very high pressure into a desired shape, analogous to the process of powder metallurgy; to conduct the firing at a rate of temperature rise as rapid as possible; and during the firing to ensure that the atmosphere surrounding the article is rich in hydrocarbons, especially unsaturated hydrocarbons. But it so happens that all these strength-promoting factors tend, whether separately or in combination, to produce swelling if they are allowed to operate without restriction.

It has now been found, however, that a strong unswollen product can be made by a careful and balanced choice of these strength-promoting factors and the use of a suitable proportion of an

appropriate swell-inhibiting agent. Adequate strength can be produced by the use of some only of the strength-promoting factors, whilst swelling can be prevented by the use of the swell-inhibiting agent and by controlling the rate of temperature rise during firing.

It has in fact been found that this process can readily result in products having a tensile strength exceeding 3,000 lbs. per square inch and a modulus of rupture exceeding 5,000 lbs. per square inch.

(8) *Electroplating*.—As the resulting products are electrically conducting, they may be electroplated.

(9) *Glazing*.—The products may be glazed and this is particularly useful where the products are intended to replace earthenware or pottery. In some cases it may be desirable to treat the products with a wetting agent appropriate to the particular glaze. With a view to extending the range of glazing materials which can be applied, the swell-inhibiting agent may be so selected as to ensure that the surface of the products will take the required glaze.

Some examples of the practice of the invention employing a chemical swell-inhibiting agent will now be given.

*Example I*.—98 parts by weight of a strongly coking Welsh coal having a volatile content of 24% and of swelling number 9, containing 8% ash (90.4% carbon, 4.9% hydrogen, 1.9% nitrogen, and 2.8% oxygen and errors on Parr's basis) was comminuted so as to pass through a 240 mesh B. S. sieve. 2 parts by weight of crystalline iodine which had been separately comminuted to the same degree of fineness was employed as the swell-inhibiting agent, and the coal and iodine powders were thoroughly mixed in a ball mill for eight hours after a preliminary mixing, in which the iodine was mixed in a ball mill for one hour with about twenty parts of the coal, the remainder then being added.

The mixture was then moulded cold into small bars about 3" long by  $\frac{1}{2}$ " wide by  $\frac{1}{2}$ " deep, under a pressure of 3 tons per square inch, the pressure being applied slowly (for example a travel of 1 inch in 10 seconds) and then immediately released. The bars were then placed in a copper box inside an electrical furnace and covered all over with a high volatile non-caking coal of a size to pass through a  $\frac{1}{8}$ " mesh B. S. sieve. The temperature of the furnace was raised to 800° C. at a rate of 1° C. per minute. The furnace was then allowed to cool and the bars were removed from the furnace when the temperature had fallen to about 250° C.

The bars were strong, unswollen and undistorted.

*Example II*.—98.5 parts of the same coal as in Example I was comminuted the same as in Example I. 1.5 parts of elemental sulphur of the fineness commonly sold as "flowers of sulphur" was employed as the swell-inhibiting agent, and the coal and sulphur were thoroughly mixed in a ball mill for eight hours, after a preliminary mixing in which the sulphur was mixed in a ball mill for one hour with about fifteen parts of the coal, the remainder then being added. The moulding and subsequent firing of bars made from this mixture was as described in Example I, and the product was the same.

*Example III*.—Coal of the same characteristics as in Example I was comminuted to the same degree of fineness as in Example I, and then moulded cold into small bars about 3" long and of about

$\frac{1}{4}$ " square cross section, under a pressure of 3 tons per square inch. The bars were then placed on a firebrick support inside an electrical furnace, and a current of ammonia gas from a cylinder was passed over the bars during the firing process. The temperature of the furnace was raised to 800° C. at a rate of 1° C. per minute, and in order to economise ammonia, the cooling was conducted in a current of oxygen-free town gas. (Note.—It would have been possible to delay the introduction of ammonia until the temperature had risen to 200–300° C. at the outset, but this was not done for reasons of convenience.) The flow of ammonia was approximately such that the volume of the furnace was supplied six times per hour. As in the previous examples, the bars were strong, unswollen and undistorted.

We claim:

1. The process of producing useful shaped articles which comprises preparing an intimate mixture of finely-comminuted coal which contains volatiles in the proportion of about 13 to 30 per cent on a dry ash-free basis with sulphur, moulding from the resultant mixture an article of the desired shape under a pressure of the order of at least two tons per square inch, at least sufficient to enable the shaped article to be transferred undamaged from the moulding machine to a furnace, releasing the pressure, producing test pieces from said mixture, firing the test pieces in a non-oxidizing atmosphere to a temperature of at least 550° C. and controlling the rate of firing in such manner as to produce a fired test piece free from cracks and free from a cellular structure visible to the naked eye, thereafter firing the moulded article under the conditions and at the rate at which the last named test piece was fired to produce an article having the properties of the fired test piece and cooling the article in a non-oxidizing atmosphere.

2. The process of producing useful shaped articles which comprises preparing an intimate mixture of finely-comminuted coal which contains volatiles in the proportion of about 13 to 30 per cent on a dry ash-free basis with a swell inhibiting agent containing a member of the sixth group of the periodic system which can generate a volatile hydride at a temperature within the firing temperature range, moulding from the resultant mixture an article of the desired shape under a pressure of the order of at least two tons per square inch, at least sufficient to enable the shaped article to be transferred undamaged from the moulding machine to a furnace, releasing the pressure, producing test pieces from said mixture, firing the test pieces in a non-oxidizing atmosphere to a temperature of at least 550° C. and controlling the rate of firing in such manner as to produce a fired test piece free from cracks and free from a cellular structure visible to the naked eye, thereafter firing the moulded article under the conditions and at the rate at which the last named test piece was fired to produce an article having the properties of the fired test piece and cooling the article in a non-oxidizing atmosphere.

3. The process of producing useful shaped articles which comprises preparing an intimate mixture of finely-comminuted coal which contains volatiles in the proportion of about 13 to 30 per cent on a dry ash-free basis with a swell-inhibiting agent containing a member of the fifth group of the periodic system which can generate a volatile hydride at a temperature within the firing temperature range, moulding from the resultant mixture an article of the desired shape

under a pressure of the order of at least two tons per square inch, at least sufficient to enable the shaped article to be transferred undamaged from the moulding machine to a furnace, releasing the pressure, producing test pieces from said mixture, firing the test pieces in a non-oxidizing atmosphere to a temperature of at least 550° C. and controlling the rate of firing in such manner as to produce a fired test piece free from cracks and free from a cellular structure visible to the naked eye, thereafter firing the moulded article under the conditions and at the rate at which the last named test piece was fired to produce an article having the properties of the fired test piece and cooling the article in a non-oxidizing atmosphere.

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