106. COMPOSITIONS, COATING OR PLASTIC.
75

Cross Reference

Examiner

Nov. 16, 1937. R. G. LEMMERMAN 2,099,342

REFRACTORY

Filed June 29, 1934

Sand, Shale, Water-glass, & Ferrous sulphate.

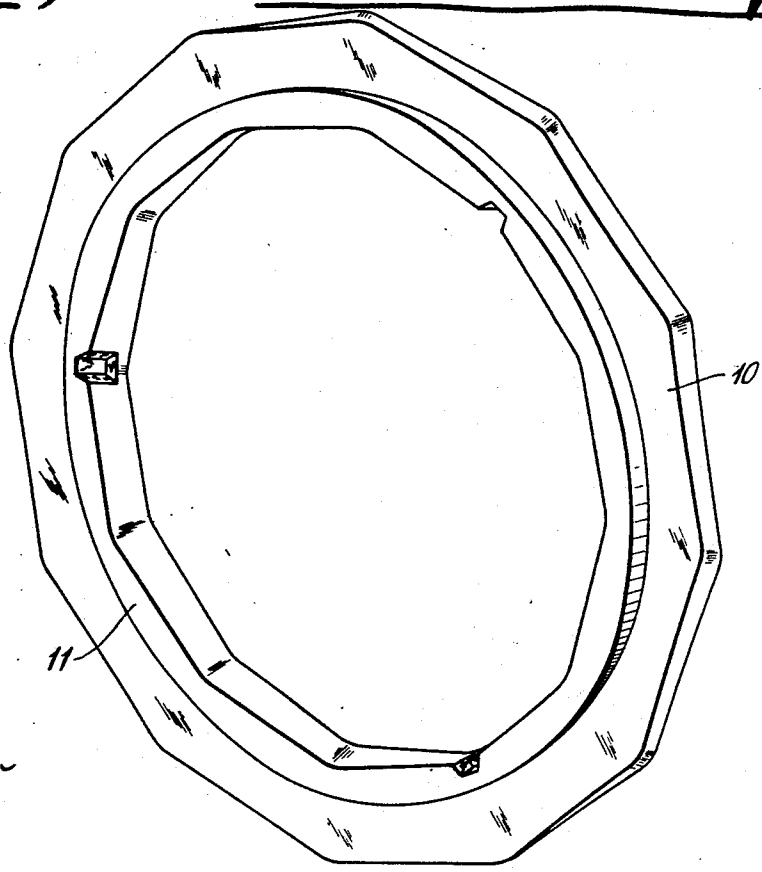


FIG. 1

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REFRACTORY

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4 Claims. (Cl. 106—9)

This invention relates to improvements in refractories, particularly refractories which are intended for use in contact with molten iron or steel, for example hot top refractories. The invention also has application however to various molded articles not intended to be subjected to high heat.

One of the objects of the invention is the provision of a refractory employing soluble silicate as a binder, which shall be moisture-proof to a large degree, that is one which shall be capable of being stored for a long period of time without taking up an appreciable amount of moisture, and consequently one which will retain its original hardness and strength indefinitely.

Another object is the production of a refractory of this character which may be subjected to sudden temperature changes over a wide range without cracking or breaking.

A further object is the production of such a refractory principally from raw material, as distinguished from manufactured materials, and hence at low cost.

Other objects and features of novelty will appear as I proceed with the description of the invention.

The single figure of the accompanying drawing is a perspective view of a bottom ring for a hot top, which constitutes an example of a refractory article embodying the invention.

In the drawing I have shown the application of the invention to bottom rings for hot tops employed upon ingot molds, that is to say lining rings for the protection of the lower ends of the hot top casings, and for insulation purposes. These rings are of course subjected to the action of molten steel, and it is important that they should be able to withstand the high heat of the metal without spalling or breaking, because the dropping of refractory material into the metal might ruin a costly ingot. It is furthermore important that these rings have good heat insulating properties in order that the metal when poured may remain molten in the hot top, and particularly at the lower end of the hot top, for a period long enough to effectively prevent piping in the ingot proper. Good functioning of the hot top in this respect appreciably increases the yield and hence decreases the cost of the steel produced.

The ring herein illustrated constitutes one element of a lining for a hot top casing. The other elements may or may not be constructed of the same refractory.

Refractory rings for the purpose above mentioned have been constructed heretofore by the methods and of the materials described in Charman and Ward Patents Nos. 1,956,894 and 1,956,895, and in my copending application Serial No. 713,151, filed February 27, 1934. In certain cases a manufactured product, that is to say zinc oxide or the like, has been used to render the molded rings moisture-proof. I have now discovered that by substituting a certain natural or raw material for a portion of the sand used in the rings previously manufactured, I can obtain equally good water-proofing characteristics, while considerably improving the heat insulating qualities and materially reducing the weight of the article, all at a lesser cost.

As in my previous application, I employ a suitable aggregate, preferably silica sand of a relatively fine grade, washed to remove impurities. Other materials mentioned in the said application may be substituted for the sand, provided they are chemically inert to the binder. As a binder I prefer to use a soluble silicate, preferably sodium silicate water glass having a water content of 60% to 65%.

The sand or other aggregate forms by far the greater proportion of the material used in the previously manufactured rings. In accordance with the present invention I replace a considerable portion of it with a shale, which must be free from oil and also free from sulphur. For this purpose I prefer to use a certain oil bearing shale which has been burned to remove the oil, this material being known to the trade as Haydite. The shale in fact constitutes a part of the aggregate, but it is not chemically inert to the water glass. On the contrary, some of its ingredients combine with the water glass in such manner as to render moisture-proof articles molded from the composition and then dried.

If the shale be an oil bearing shale, as is Haydite, the burning operation is performed, driving off the oil and leaving the particles quite porous. On account of this porosity the volume of the material for a given weight is much greater than that of sand. I crush this material before using it.

The chemical analysis of Haydite, which is an example of a shale that is well suited to the purpose, is as follows:

	Percent
Silica (S_iO_2)	65.40
Alumina (Al_2O_3)	12.30
Iron oxide (Fe_2O_3)	13.30
Lime (CaO)	5.20
Magnesia (M_gO)	2.77
Alkalies ($AsNa_2O$)	0.65

I have found that when a shale of this kind in proper proportions is thoroughly mixed with sand and made up into molded articles with a water glass binder, the resulting articles have much greater strength than does the shale and water glass alone, and that they have much better heat insulating qualities than does sand and water glass alone. The water-proofing qualities of the material are apparently due to the presence of the metallic oxides. The insulating qualities are due in part, at least, to the pores left by the burning off of the oil.

The relative proportions of shale and sand may vary considerably, that is to say anywhere from 5% shale and 95% sand to 80% shale and 20% sand. The strength improves to some extent with an increase in the proportion of sand, and the insulating qualities improve materially with an increase in the proportion of shale. At the present time I prefer a mix in which shale and sand are in the proportion of 40% and 60%. This gives a strong ring and one having insulating properties equal to those of brick. It is also highly resistant to moisture and hence remains hard in storage.

When the rings as heretofore constituted are subjected to the heat of molten metal the dry silicate binder tends to fuse, with the result that the rings lose most of their strength. In the rings of the present invention the same tendency is present, but the heat of the molten metal also tends to soften the shale, and this softened shale forms a mechanical bond which is highly effective.

When the shale and sand are thoroughly mixed, water glass in the proportion of 6% to 20% by weight of the entire mass is added, together with water, and the mixing resumed until all of the ingredients are intimately commingled. The articles to be manufactured are then molded and compacted, after which they are dried in an oven. The temperature of the drying oven may vary with the length of time the molded article remains in the oven. It should be high enough to drive off the moisture, but not high enough to vitrify the material and destroy the binding qualities of the silicate.

Refractories made in accordance with the foregoing method are quite water resistant, and may be stored for a reasonable time without absorbing an appreciable amount of moisture. However, I prefer to add to the mix a very small quantity of a soluble sulphate, preferably ferrous sulphate. Other sulphates which may be substituted for the ferrous sulphate are ferric sulphate, and sulphates of the following metals: zinc, copper, lead and aluminum.

The quantity of the sulphate to be used is very small comparatively, and bears a direct relation to the quantity of silicate. Since the quantity of silicate in the molded article may vary between fairly large limits, it is difficult to prescribe limits for the sulphate. It is important, however, to note that the quantity of sulphate for any given silicate content must not exceed a certain critical point, which is in the neighborhood of 5% or 6% by weight of the soluble silicate solution. This proportion is based upon the use of sodium silicate water glass having a water content of 60% to 65%. Below such critical point the water-proofing effect of the sulphate increases as the quantity increases. A material excess of sulphate above the critical point has a deleterious effect upon the binding qualities of the silicate.

The precise effect of the ferrous sulphate or its equivalent in this method is somewhat open to conjecture. It may be that it unites with the soluble silicate to produce an insoluble silicate, or it may be that it acts as a promotor for other chemical reactions. At any rate, the sulphate has an important effect upon the product in that it assists in the water-proofing of the product.

In a 1000 pound batch the weights of the different ingredients may be said, by way of example merely, to be as follows:

Sand or other aggregate	480 lbs. or 48%
Haydite	320 lbs. or 32%
Water glass	177 lbs. or 17.7%
Water	20 lbs. or 2%
Ferrous sulphate	3 lbs. or .3%

After drying, the make-up of the molded article when made from the above ingredients in the proportions stated will be substantially as follows:

	Per cent
Sand or other aggregate	56
Haydite	37
Dry silicate equivalent	7

In the foregoing description I have necessarily gone somewhat into detail in order to explain the invention fully, but I desire it to be understood that such detailed disclosures are not to be construed as amounting to limitations except as they may be included in the appended claims.

Having thus described my invention, I claim:

1. A molded and dried refractory having a water glass binder, said refractory comprising shale burned to provide porosity and an aggregate chemically inert to the water glass, said shale and aggregate constituting together from 90% to 99% by weight of the entire refractory.

2. A molded refractory which comprises the following ingredients in the following proportions by weight: silica sand from 11% to 94%, shale burned to provide porosity from 5% to 80%, and dry alkali silicate from 1% to 9%.

3. A refractory comprising the following ingredients in approximately the following proportions by weight, aggregate and shale together 93%, said shale being burned to provide porosity, and dry alkali silicate 7%.

4. A refractory body in molded and dried form comprising sand and the burned porous residue of an oil-bearing shale which contains a substantial proportion of metal oxide, and an added alkali silicate binder, said shale residue being capable of combining with the silicate when the body is dried to form a composite binder for the sand.

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