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STOPPER HEADS

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This invention relates to improvements in stoppers or stopper heads such as are used for controlling the flow of metal from steel ladles and the like, and is a continuation in part of my copending application, Serial No. 154,893 filed April 8th, 1950, now abandoned in favor of this application.

It is the usual practice in the handling of molten steel to control the flow of the metal from a refractory lined ladle by forcing a so-called stopper or stopper head into contact with a perforate refractory nozzle thru which the molten metal flows when the stopper is raised out of contact with it. The stopper may be alternately raised and lowered many times in the processing of a ladle full of molten metal and it is essential that each time it is reseated on the nozzle, the metal be shut off promptly and fully. The stopper head itself is held in place by a steel stopper pin inserted axially through the stopper and itself attached to a long steel tube or rod which is used to force the stopper down against the nozzle. This steel tube and the pin are protected from the molten metal by a refractory sleeve surrounding them and by the stopper itself. It is thus important that the stopper be not only highly refractory but that it be of low thermal conductivity to retard the flow of heat through it to the pin, lest the pin become so highly heated as to cause it to fail, releasing the stopper and rendering the whole assembly useless. Even if over-heating of the pin does not cause its complete and immediate failure, overheating may still damage it to an extent which prevents its re-use in subsequent stoppers so that it is definitely desirable that the stopper permit a minimum flow of heat through it to the pin.

There is, however, an even more important factor to be considered in stopper heads which is readily apparent when the nature of their service is considered. The ladle with the relatively cold stopper in place is suddenly filled with molten metal, at temperatures of 2900° F. to 3100° F. or even higher, which metal surrounds the stopper on all sides and subjects it to tremendous thermal shock which is sufficient to crack or break most ceramic bodies. Such cracking may seriously impair the ability of the stopper to perform its intended function and indeed cause immediate failure and disastrous accidents.

It is the purpose of my invention to provide stopper heads which are refractory and extremely resistant to such cracking by thermal shock, and which are chemically inert so that they do not react with the materials with which they come in contact during use. In other words, my invention produces stopper heads which are phenomenally dependable in service by virtue of resisting each of the destructive forces which ordinarily results in premature trouble from the stopper.

An excellent discussion of stoppers and their use in the steel industry appears in the Open Hearth Proceedings of the A. I. M. E. for 1945, pages 121 to 153. In that publication, engineers of the Carnegie Illinois Steel Co. point out the serious effects which may result if a stopper head cracks open or shells off as a result of contact with the molten steel. Such failures constitute a serious hazard

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to the safety of the workmen and may result in loss of metal, spoilage of accessory equipment or in inferior castings. The Carnegie Illinois investigators state that every type of stopper head tested showed cracking of greater or less seriousness when the stopper was immersed in molten steel. The expensive nature of the trouble resulting from any leakage has led to the practically universal practice of throwing away all stopper heads (and sometimes the pins too) after use in only one ladle of steel. This is expensive but far cheaper than having the molten metal fail to shut off cleanly at some critical time.

Stopper heads have for many years been made out of a mixture of clay materials plus a certain amount of graphite which is reputed to impart to the body a sort of internal yieldability or flexibility under the heavy pressures applied in service. A characteristic composition would be:

20 parts by weight of ball clay
4 parts by weight of bentonite
13 parts by weight of clay grog thru 8 mesh
25 parts by weight of clay grog thru 14 mesh
18 parts by weight of Ceylon graphite
10 parts by weight of crushed scrap stoppers

Such a mixture is wet up with enough water to permit the mass to be formed into desired shapes either by dry pressing or by plastic forming methods familiar in the art. The material is shaped by one of these methods into heads having the sort of perforate ball shape well known to stopper users and these are thereafter dried and fired in the method common to the ceramic industry.

Attempts have been made in the past to utilize as stoppers bodies consisting principally of graphite, carbon, silicon carbide, etc., but these materials have proved entirely unsuited due in part to their chemical reactivity with the molten metal and in part to their high thermal conductivity which has resulted in burning off the supporting pins. Stoppers formed principally of clay materials have been successful but have been characterized by universal spalling trouble as above described.

I have discovered that highly successful stoppers can be made by incorporating in stopper mixes of the usual type a relatively small proportion of a ceramic grog having a low coefficient of thermal expansion, i. e., below about 2.7×10^{-6} per degree centigrade. Examples of such grogs are:

Material:	Linear coef. exp./°C.
Lithium zirconium silicate ($\text{Li}_2\text{O} \cdot \text{ZrO}_2 \cdot \text{SiO}_2$)	2.7×10^{-6}
Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) calcined to 1100° C.	2.5×10^{-6}
Beta spodumene, calcined to 1100° C.	1.9×10^{-6}
Petalite, calcined to 1100° C.	1.9×10^{-6}
Beryl	1.0×10^{-6}
Quartz glass (fused silica)	0.6×10^{-6}

The coefficients of expansion shown are those found in applicant's experience with materials actually used when calcined as indicated.

While I find that any of these materials can be used in accordance with my invention to produce stopper heads with improved resistance to heat shock, I prefer to use fused silica on account of its high refractoriness which permits it to be kept submerged in the very hot steel without danger of fusion while the ladle is being emptied.

It is, of course, desirable, in order to keep cost down, to limit the proportion of these high priced ingredients so far as practicable and I have found that in clay-graphite bodies of the type herein described non-spalling characteristics begin to be imparted with as little as 10% of

a low expansion grog and are very strongly evident in bodies containing 12% to 15% by weight of fused silica for example. Still higher percentages can be used without inducing spalling but the use of more than 30% is usually not desirable both because of needless cost and because the thermal conductivity of the stopper with higher proportions of the low expansion grog becomes so high as to result in damage to the stopper pins.

The fused silica or other low expansion grog should be relatively free from material finer than 70 mesh size. It should, on the other hand, all pass an 8 mesh screen. The exact sizes within this range are not critical. Grog of the types enumerated above, when in particle sizes finer than 70 mesh, tend to be so affected by prolonged heating as to alter their structure and cause them to lose their low coefficient of expansion but such finer grog may be used to reduce the amount of clay grog otherwise required.

As for the other ingredients, the bond clay may be any refractory plastic clay. It should be used in sufficient proportion to render the body easily formable. In general, from 15 to 50% by weight works out well. The clay grog (as distinguished from the low expansion grog) should likewise usually run from 15 to 50% by weight of the total mix though less may be used where the clay does not shrink excessively on firing. It may vary within any convenient grit size limits, such as 35 mesh and finer or 8 mesh and finer. The sum of the clay materials (clay and grog) may appropriately be from 50 to 70% of the weight of the entire body. I have found it advantageous at times to add to the mix a quantity of fine aluminum oxide or material consisting of over 60% alumina such as kyanite fines, up to perhaps one fourth the weight of the clay and clay grog present so as to raise the alumina content of that portion of the mix and make the stoppers more refractory and inert at high temperatures.

The graphite content should be kept low for reasons of economy but I have found from 12 to 20% of flake graphite to be desirable in my stopper bodies. This flake graphite should be substantially all finer than 10 mesh and at least half of it coarser than 100 mesh. It may comprise a range of grit sizes but need not be of any special size within the stipulated range. I prefer to use graphite, the free carbon content of which is from 75 to 85% and the "tap" packing density of which is around 0.75 to 0.85 gms. per cc.

I recite the following representative mixes by way of illustration but do not wish to be limited thereby (all percentages by weight):

Formula 1

	Percent
Fused silica, 8 mesh and finer.....	44
Madagascar flake graphite.....	17
Klingenberg clay.....	39

Formula 2

	Percent
Firebrick grog, 35/60 mesh.....	17
Raw kyanite, 100/finer mesh.....	13
M & D ball clay.....	36
Cordierite (1100° Calcine), 8/35 mesh.....	14
Madagascar flake graphite.....	20

Formula 3

	Percent
Firebrick grog, 35/finer mesh.....	20
Fused silica, 16/35 mesh.....	14
Fused silica, 8/16 mesh.....	10
"Stopper fines" graphite.....	17
Ball clay.....	14
Karblite clay.....	21
A-2 calcined alumina.....	4

Formula 4

	Percent
Firebrick grog, 8/finer mesh.....	30
Fused silica, 8/16 mesh.....	3
5 Fused silica, 16/35 mesh.....	4
Fused silica, 35/70 mesh.....	7
Kaolin.....	9
Ball clay.....	33
A-2 calcined alumina.....	4
10 Flake graphite.....	10

Klingenberg clay is a well known refractory German ball clay.

Firebrick grog means crushed burned firebrick. It is composed of relatively pure aluminum silicates, sometimes plus free silica and alumina and is a term familiar in the ceramic industry.

M & D ball clay is a typical Mississippi ball clay as sold by the Kentucky Tennessee Clay Company of Mayfield, Kentucky. A typical analysis is:

	Percent
SiO ₂	57.0
Al ₂ O ₃	27.9
Fe ₂ O ₃	2.2
25 TiO ₂	1.3
Alkalies.....	1.3
Ignition.....	9.8

Stopper fines graphite designates natural flake Madagascar graphite too fine in size for the most demanding crucible trade which is imported by various concerns and sold to the producers of stopper heads in the U. S. under this name.

Karblite clay is a typical Tennessee ball clay produced by the Bell Clay Company of Gleason, Tennessee. A typical analysis is:

	Percent
SiO ₂	55.0
Al ₂ O ₃	30.9
Fe ₂ O ₃	0.9
40 Alkalies.....	2.1
Ignition.....	11.2

"A-2" calcined alumina is a very fine powdered calcined alumina sold by the Aluminum Company of America under that designation. It contains over 99% 45 Al₂O₃ with up to ½ % Na₂O.

The ingredients of such formulas as the foregoing should be mixed together with sufficient water to make the material moldable by ordinary ceramic methods and then formed in the way stoppers are usually formed. 50 Then after careful drying, the molded stopper heads should be buried in graphite or other granular carbon and, while so buried, fired to a temperature sufficient to vitrify the clay binder. This is important as the stopper is dangerously weak if it is not fired hot enough to vitrify it. The necessity for firing adequately high to develop strength is well recognized in the stopper art but until my present invention such firing had been accompanied by a serious increase in the tendency of the vitrified stoppers to spall in service. In the case of the examples cited, firing to Cone 9 (1250° C.) for four hours followed by a flash fire to Cone 11 (1285° C.) has been found satisfactory. Too long firing at too high a temperature is apt to devitrify fused silica and should be carefully avoided in the processing of stoppers containing this material. Clays should be selected which do not require firing above temperatures at which they will react with the low expansion grog used.

In service, these stoppers show no cracks whatever after use. They exhibit excellent resistance to erosion 70 by the molten steel even in unusually corrosive melts such as nickel chromium steel and high carbon steel or steels high in manganese and sulfur which are notoriously hard on stoppers. Heads taken out of service after use in pouring 130 tons of metal past them looked capable of reuse. As indicated above, the stopper pins were

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found to be in better condition after use in stoppers containing 30% or less of fused silica than in those made of Formula 1 for example, but even the latter performed adequately.

Having thus explained my invention and given several examples of its application, what I claim is:

1. A raw mix for the manufacture of stopper heads, said mix consisting of from 15 to 50% by weight of a plastic refractory clay, 15 to 50% by weight of refractory clay grog and from 12 to 20% by weight of flake graphite and comprising from 12 to 20% by weight of fused silica.

2. A stopper head composed of from 12 to 20% by weight of flake graphite, from 12 to 30% by weight of fused silica and 50 to 70% by weight of fired refractory clay.

3. A stopper head consisting of from 12 to 20% by weight of flake graphite, 12 to 30% by weight of fused silica, from 50 to 70% by weight of fired refractory clay and additional aluminum oxide up to one fourth the weight of said clay.

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4. A stopper head composed of from 15 to 20% by weight of flake graphite, from 12 to 15% by weight of fused silica and the remainder fired refractory clay.

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