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PROCESS OF PRODUCING A FOUNDRY CORE COMPOSITION

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This invention relates to foundry cores and in particular to a process of producing a foundry core composition.

A foundry core may be defined as that part of shaped sand and binding material that aids in forming an internal part of a metal casting. There are several requirements for a foundry core. It must usually cure rapidly; it must resist the washing and burning action of a stream of hot metal; it must admit of the free escape of gases; it must impart its internal contour to the metal casting; it must have sufficient tensile strength so that it is not ruptured while being handled or worked; and finally it must shake out readily after the metal casting has hardened.

To satisfy some of these requirements the foundry art has long employed sand along with a suitable binder. A binder may be defined as that part of the foundry core composition which causes adhesion among the sand particles. In the following description the term "binder" will include all organic ingredients of the foundry core composition.

Various binders have been used by the foundry industry. One of the oldest known binders is the cereal-core oil binder. The main disadvantage of this system is the long curing time required. Today with the use of high-speed automatic equipment a rapid curing binder is very desirable.

Another type of core binder is made from phenolic resins. Because of the high cost of such resins, the binder is used to merely bond a shell instead of acting as a binder throughout the core. The use of phenolic resin type binders results in foundry cores that have a tendency to resist shakeout after the metal casting has hardened, particularly when casting low-melting non-ferrous alloys. Also the curing time required and the tensile strengths of the resulting foundry cores could be improved.

A third type of core binder is the urea-formaldehyde-cereal binder. This system requires sufficient water to be present in order that the foundry core will have sufficient "green or wet strength" to retain its shape until it is placed in an oven. The presence of water in the required quantities increases the curing time. In addition this binder produces a core that collapses too readily on contact with high-temperature melting metals, such as grey iron. Another problem with the core produced by this binder is the lack of humidity resistance. Lack of such resistance causes the core to lose strength upon exposure to an atmosphere with high humidity.

It is an object of this invention to produce a foundry core that has an improved tensile strength.

Another object of this invention is to produce a core composition that cures rapidly so that it may be used with high-speed automatic machinery.

Still another object of this invention is to produce a foundry core which can withstand the heat from a high melting point metal and yet can be readily shaken out after the metal casting has hardened.

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A further object of this invention is to produce a foundry core from materials that are relatively inexpensive as compared to many presently used materials.

A still further object of this invention is to produce a foundry core that does not lose strength in a high humidity atmosphere.

Another object of this invention is to provide a process for producing a foundry core that permits a stable two-package system of marketing.

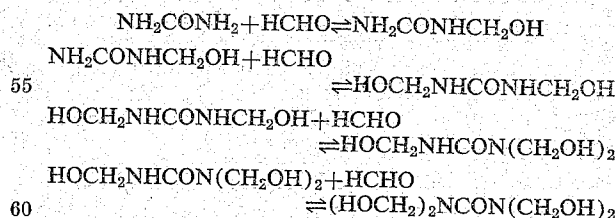
In accordance with the invention the above objects are accomplished by a process in which a first mixture including furfuryl alcohol and a non-polymerized aqueous mixture of formaldehyde, urea and equilibrium reaction products thereof (the latter aqueous mixture hereinafter referred to as an aqueous U.F. mixture) is admixed with a second mixture including urea, an acidic catalyst and sand. Five to fifty parts of furfuryl alcohol is employed in the first mixture, however, twenty-five to fifty parts is the preferred range. (All quantities stated in this description as "parts" are parts by weight and are based on a total of 100 parts to the binder, unless otherwise indicated.) Ninety to thirty-five parts of the aqueous U.F. mixture is employed. Said aqueous U.F. mixture contains at most 15% by weight of water. In the aforementioned second mixture it is essential to employ 3,000 to 10,000 parts of the sand, one to three parts of the acidic catalyst, and the urea in sufficient amount to give a molar ratio of available urea to available formaldehyde in the combined mixtures in the range of 1:1.5 to 1:2.5, preferably from 1:2.0 to 1:2.5.

In one embodiment of the invention 0.5 to 7.0 parts of aqueous ammonia (29% ammonia) are added to the ammonium salt and urea in the aforesaid second mixture.

In another embodiment in which ammonium chloride is employed as the acidic catalyst, aluminum stearate is admixed with the urea and ammonium chloride in the aforesaid second mixture in an amount 1-5% by weight of the combined weight of urea and ammonium chloride in the second mixture.

In a further embodiment 12 to 25 parts of water are admixed with the urea and ammonium chloride in the second mixture.

Aqueous U.F. mixtures are sold in commerce. One example is "U.F. Concentrate-85" sold by the Nitrogen Division of Allied Chemical & Dye Corporation, South Point, Ohio. Another aqueous U.F. mixture is made by E. I. du Pont de Nemours and Company, Wilmington, Delaware, and is marketed as "Urea-Formaldehyde 25-60." The formaldehyde, urea and equilibrium reaction products thereof, present in aqueous U.F. mixtures are believed to exist in equilibria as follows:



The above equilibria illustrate what is meant by the phrase "a non-polymerized aqueous mixture of formaldehyde, urea and equilibrium reaction products thereof." Those urea molecules in the equilibria shown above that have more than one methylol radical attached are some-

times referred to as polymethylol ureas. There is difficulty encountered in distinguishing between the different polymethylol ureas in the aqueous U.F. mixtures. For this reason the composition of the aqueous U.F. solution is reported in terms of the weight percent urea and formaldehyde. A typical analysis of Allied Chemical's aqueous U.F. mixture ("U.F. Concentrate-85") shows 59% by weight formaldehyde, 26% by weight urea, and at most 15% by weight water.

The total amount of urea and formaldehyde present in the final mixture (the combination of the first and second mixtures) is stated in terms of a molar ratio. The parts of urea included in the second mixture varies with the analysis of the particular aqueous U.F. mixture that is employed in the first mixture. Thus the parts of powdered urea included in the second mixture can be determined with the aforementioned molar ratio, given the analysis of a particular aqueous U.F. mixture.

The term "available urea" refers to free urea as well as urea combined with the methylol group in the equilibria shown above. The term "available formaldehyde" refers to free formaldehyde as well as formaldehyde combined with urea in the equilibria shown above.

The amount of acidic catalyst employed in the second mixture will vary within the stated range depending upon the type of sand used and also the curing properties that are desired. Sands with a high clay content may have a high acid demand and require more acid catalyst. Generally any acidic catalyst may be employed, e.g., ammonium chloride, ammonium trichloroacetate, ammonium dihydrogen phosphate, ammonium sulfate and ammonium nitrate. Ammonium salts of a strong acid are particularly well adapted to use as a catalyst in this invention.

With approximately 100 parts binder, 3000 to 10,000 parts of foundry sand are used. The sand employed in the working examples shown below was a clean lake sand with an AFS (American Foundry Society) fineness of about 83. However, any of the commonly used foundry sands are suitable.

In commercial practice, foundries employing this invention are provided the aforementioned first mixture in a single package. The aforementioned second mixture minus the sand is provided in a second package. The sand in the specified proportion is then admixed with the second package at the foundry to constitute the aforementioned second mixture. By this procedure a 2-package system is provided in which each package is stable throughout the usual shipping and storage times.

Various additional components may be added to the urea and catalyst in the second mixture. The aforementioned addition of ammonia gives considerable improvement in storage life with little sacrifice in curing speed. The aforementioned addition of aluminum stearate prevents the caking of the powdered urea. The aforementioned addition of water gives improved catalyst distribution.

The invention will be further illustrated but is not limited by the following examples:

Example 1

A first mixture was prepared by blending 17.8 parts of "U.F. Concentrate-85" with 9 parts of furfuryl alcohol. Six parts of powdered urea were admixed with 0.30 part of ammonium chloride and then admixed with 1000 parts of sand to form a second mixture. The first mixture was then admixed with the second mixture which resulted in a final mixture of all the aforementioned constituents. This final mixture had 30 parts of furfuryl alcohol in its binder portion. In the same manner 4 additional final mixtures were made up with 10, 20, 40, and 50 parts respectively of furfuryl alcohol in the binder portion. The formaldehyde-urea molar ratio in these 5 final mixtures was 2. Twenty-five gram samples of the final mixtures were rammed three times with a Dietert rammer

into dog-biscuit shaped molds. This produced ¼ inch thick specimens which were formed directly on aluminum plates. These specimens were transferred from aluminum plates to a hot plate in an oven at 425° F., where they were cured for varying lengths of time and tested at 5 second intervals. The time at which the specimens were hard when removed from the oven was taken as the normal curing time. The following results were obtained:

Specimen No.	Parts of Furfuryl Alcohol in Binder	Curing Time (Seconds at 425° F.)
1.....	10	25
2.....	20	25
3.....	30	30
4.....	40	30
5.....	50	30

It is apparent that the effect of a variance in the furfuryl alcohol concentration on the curing time of the core binder is slight.

Additional specimens produced from the aforementioned five final mixtures were cured for the curing times shown above. Tensile strength tests were then made. The reported strength data were averages of five tests in each case. The results, reported in pounds per square inch (p.s.i.), were as follows:

Specimen No.	Parts of Furfuryl Alcohol in Binder	Tensile Strength of Foundry Core (Normal Curing Time) p.s.i.
6.....	10	305
7.....	20	440
8.....	30	540
9.....	40	590
10.....	50	580

The strength of the baked cores was approximately doubled by substitution of furfuryl alcohol for 20% by weight of the resin in the binder and strength increased linearly when employing up to 30% furfuryl alcohol by weight.

In making foundry cores the thicker bodied cores often require a more intensive cure in order that internal areas will sufficiently cure. This may result in the surface being overcured. To ascertain the effects of overcure on the composition produced by this invention, additional specimens prepared by the method outlined above were overcured for 20 seconds. The following results were obtained:

Specimen No.	Parts of Furfuryl Alcohol in Binder	Tensile Strength of Foundry Core (Overcured) p.s.i.
11.....	10	200
12.....	20	---
13.....	30	420
14.....	40	550
15.....	50	580

If the tensile strengths of the cores with a normal cure and an overcure are compared, it is apparent that with higher concentrations of furfuryl alcohol (40-50 parts), the 20 second overcure has little effect on decreasing the tensile strengths. With the danger of surface overcure somewhat minimized by the addition of larger amounts of furfuryl alcohol, a greater amount of heat can be applied to effect the cure throughout the body of the core.

Example 2

The procedure for making up the final mixtures in Example 1 was repeated except that the parts of furfuryl

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alcohol remained constant at 20 parts while the molar ratio of available formaldehyde to available urea was varied in each of 4 final mixtures. In addition 0.18 part of aluminum stearate were added to the urea and ammonium chloride in the second mixture. The following foundry core tensile strengths were obtained:

Specimen No.	Molar Ratio of Formaldehyde to Urea	Tensile Strength of Foundry Cores (p.s.i.)
1-----	1.25	255
2-----	1.50	350
3-----	1.75	450
4-----	2.0	440

The data shows that as the formaldehyde-urea molar ratio increased up to 1.75, there was an increase in the tensile strength of the foundry core.

Example 3

The procedure for making up the final mixtures in Example 1 was repeated except that the parts of furfuryl alcohol were held constant at 30 parts, while the parts of binder in relation to the sand were varied as shown below. The tensile strengths of the different specimens of foundry cores were as follows:

Specimen No.	Parts by Weight of Binder	Tensile Strength of Foundry Core (p.s.i.)
1-----	1.0	200
2-----	1.5	320
3-----	2.0	485
4-----	2.5	495
5-----	3.0	530

Example 4

The procedure for making up the final mixtures was repeated as in Example 1, except that the furfuryl alcohol content was 30 parts for all 5 of the final mixtures. In addition varying quantities of ammonia (as 29% aqueous solution) were added. The final mixtures were not placed into molds as in Example 1, but instead glass beakers with aluminum foil covers were half filled with the final mixtures. These beakers were placed in an oven at 120° F. During the course of these tests, the final mixtures crusted over after a few minutes, while the material in the bottom was still usable. The mix life which is a measure of the stability of final mixtures, was taken as the time when the material in the bottom began to harden. The samples were examined every ten minutes. The following data on mix life and curing time was obtained:

Specimen No.	Parts of Aqueous Ammonia (29% NH ₃)	Mix Life Stability (Minutes at 120° F.)	Curing Time (Seconds at 425° F.)
1-----	0.0	50	30
2-----	0.54	70	30
3-----	1.07	100	35
4-----	1.60	160	35
5-----	2.14	180	45

Thus by the addition of the ammonia, considerable improvement in mix life is obtained with little sacrifice in the curing time.

Example 5

The procedure in Example 1 for making up the final mixtures was repeated except that 20 parts of furfuryl alcohol were used and the molar ratio of formaldehyde to urea was varied in each of 4 final mixtures. The time interval at which the specimens were hard when

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removed from the oven was taken as the curing time. The following results were obtained:

Specimen No.	Molar Ratio of Formaldehyde to Urea	Curing Time (Seconds at 425° F.)
1-----	2	25
2-----	1.75	30
3-----	1.50	30
4-----	1.25	40

Thus, as the molar ratio of formaldehyde to urea decreases, there is an increased curing time required.

Example 6

The procedure for making up the final mixtures in Example 1 was repeated except that 30 parts of furfuryl alcohol and 3 parts of various catalysts were used in the final mixtures. In addition 25 parts of water were admixed with the urea and ammonium chloride catalyst in the second mixture. The curing time of the foundry cores and their tensile strengths were taken in the manner previously described. The results obtained were as follows:

Catalyst	Curing Time (Seconds at 425° F.)	Tensile Strength of Foundry Core (p.s.i.)
Ammonium trichloracetate-----	25	480
Ammonium nitrate-----	30	500
Ammonium sulfate-----	25	210
	30	240
	30	230
	40	620
Ammonium dihydrogen phosphate-----	50	650
	40	380
	45	560
	50	650

Example 7

Fifty-eight parts of "U.F. Concentrate-85" and 42 parts of furfuryl alcohol were admixed to form the "first mixture" of this invention. Eighty-six parts of powdered urea, 11 parts of ammonium chloride and 2.6 parts aluminum stearate were dry mixed, and then 24 parts of this dry mixture were added to 12,000 parts of sand and mulled for two minutes to form the "second mixture" of this invention. Eighteen parts of water were then added to the second mixture to give a mixture hereinafter referred to as "modified second mixture" (i.e., modified by the presence of water as well as aluminum stearate). The modified mixture was mulled for two minutes. One hundred and fifty-five parts of the first mixture were then added to the modified second mixture and the two mixtures mulled to form a final mixture with a urea-formaldehyde ratio of 2.5 to 1.

The final mixture was used to make foundry cores and were tested for tensile strengths as in Example 1. Tensile strengths of 360 p.s.i. were obtained. The use of the water resulted in improved uniformity of the mixture and improved catalyst distribution. Thus, where a hot core box was used to initiate the curing and the foundry core was removed and allowed to stand at room temperature to complete the internal curing, a more complete cure was obtained than where water was not used in the second mixture.

It has also been found that as a supplement to the foundry core composition produced by this invention, 0.3 to 0.5 part of Methocel, carboxy-Methocel or guar gum (based on 100 parts of sand) may be admixed with the aforementioned second mixture. Then to this modified second mixture, before the addition of the first mixture, is added 3 to 6 parts of water (based on 100 parts of sand). The addition of the above ingredients will provide the core with additional green strength. The aforementioned gums are similarly useful in foundry core compositions generally.

We claim:

1. A process of producing a foundry core composition comprising the steps of:

(a) Preparing a first package including a mixture of about 5 to 50 parts by weight of furfuryl alcohol and about 90 to 35 parts by weight of a stable non-polymerized aqueous mixture of urea, formaldehyde, and equilibrium products thereof, said aqueous mixture containing at most about 15% by weight of water;

(b) Preparing a second package including a mixture of about 1 to 3 parts by weight of an acidic catalyst, and sufficient urea so as to give a molar ratio of available urea to available formaldehyde in the range of about 1:1.5 to 1:2.5 when said first package and said second package are combined; and

(c) Admixing said first package, said second package and about 3,000 to 10,000 parts by weight of sand.

2. The process of claim 1 in which said acidic catalyst is an ammonium salt of a strong acid.

3. The process of claim 1 in which said acidic catalyst is an ammonium salt of a strong acid and in which 0.5 to 7.0 parts by weight of aqueous ammonia are added to the acidic catalyst and urea in said second package, said aqueous ammonia being calculated as 29% by weight ammonia.

4. The process of claim 1 in which said acidic catalyst is ammonium chloride and in which aluminum stearate is admixed with the urea and ammonium chloride in said second package in an amount of about 1 to 5% by weight of the combined weight of urea and ammonium chloride in said second package.

5. A process of producing a foundry core composition comprising the steps of:

(a) Preparing a first package including a mixture of about 5 to 50 parts by weight of furfuryl alcohol and about 90 to 35 parts by weight of a stable non-polymerized aqueous mixture of urea, formaldehyde, and equilibrium products thereof, said aqueous mixture containing at most about 15% by weight of water;

(b) Preparing a second package including a mixture of about 1 to 3 parts by weight of ammonium chloride, about 12 to 25 parts by weight of water, and sufficient urea so as to give a molar ratio of available urea to available formaldehyde in the range of about 1:1.5 to 1:2.5 when said first package and said second package are combined; and

(c) Admixing said first package, said second package and about 3,000 to 10,000 parts by weight of sand.

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