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Porosity Defects in Iron Castings from Mold Metal Interface Reactions

by

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ABSTRACT

In the 25 years since the original paper was written, there have been considerable technical advances in foundry binder technology as well as sand mixing and processing equipment. The techniques and equipment available to the foundrymen in 1974 were rather primitive compared to today's improved binder chemistry and selection, mixing and binder metering equipment and sand reclamation technology

This paper updates the original 1974 research on porosity susceptibility of gray and ductile iron castings prepared with cores bonded with the then newly developed urethane types of no bake binders. The 1974 study was aimed at delineating the effects of core and mold making variables on porosity susceptibility and the development of remedial practices to eliminate binder-related defects when they occur. Also investigated were the effects of casting variables and how these relate to the occurrence of such defects. The updated research focused on the evaluation of current resin technology, iron oxide additions, and the effects of porosity inhibiting ferroalloys. Lastly, other unpublished research by the author during the ensuing 25 years is also included.

New and improved binder formulations of 1998 provided virtually identical casting results compared to the 1974 research. Binder ratios of polyol resin to polyisocyanate component less than one (favoring higher levels of the polyisocyanate component) tended to increase overall porosity susceptibility. Balanced or ratios (greater than one) were, in general, not susceptible to defect formation. Defect formation was enhanced by high pouring temperatures, especially when polyol to polyisocyanate ratios were less than one and when high binder levels were employed. Poor binder dispersion from sand mixing was also responsible for increasing the overall susceptibility to these types of defects. Porosity defects resulting from employment of unfavorable binder and/or casting practices could be eliminated by adding relatively small additions of red iron oxide (hematite or Fe_2O_3) to the sand mix. The use of magnetite or black (Fe_3O_4) grades of iron oxide were not nearly as effective in preventing porosity. The addition of nitrogen stabilizing elements, such as titanium and zirconium, were effective to varying degrees in eliminating porosity. Best results were obtained with additions of proprietary titanium bearing gray iron inoculants. Addition of proprietary, ferrosilicon based inoculant alloys containing either titanium or zirconium were also very effective in eliminating porosity. Additions of zirconium silicide to a new, proprietary, oxy-sulfide containing inoculant was also very effective in eliminating porosity. Other methods for eliminating defects, although not nearly as practical, were 1.) core post-baking at 450^{o}F and 2.) use of core coatings modified with red iron oxide.

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from Mold Metal Interface Reactions

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Introduction: Surface and subsurface gas defects have always been common and troublesome defects in gray iron and other castings poured in green sand molds. Within the past 30 years, however, innovations in synthetic binder technology have resulted in movement away from green sand molding and toward total no-bake molding and coremaking processes and accompanying new types of casting defects. The growth in phenolic urethane binder technology since 1970, the year phenolic urethane no-bake binders were introduced, has been phenomenal and is shown in Figure 1.

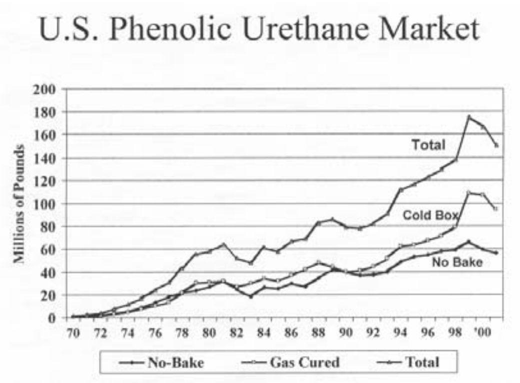


Figure 1: Phenolic Urethane Resin Consumption in the United States

When the original porosity paper was written in 1974, only 11.76 MM lbs of phenolic urethane binders were consumed by the U.S. foundry industry. In 1998, it is estimated that 137 MM lbs of these resins (3,262 truckloads, a truckload weighing 42,000 lbs.) were consumed in the United States. Estimated worldwide use is generally considered to be over 300 MM lbs. As a result of the increased acceptance and consumption of phenolic urethane binders, occurrences of binder related gas defects have at times become very troublesome in foundries using these systems.

Generally speaking, there are three major sources that may contribute to porosity formation in gray iron castings. These are: 1) high initial gas content of the melt originating from either the charge ingredients, melting practice or atmospheric humidity, 2) reaction of carbon and dissolved oxygen under certain melt conditions, and 3) mold-metal reactions between evolved mold and core gases at the solidifying casting surface.[1-16] In addition, any combination of these three sources may have a cumulative effect on promoting porosity formation. However, the gases normally held responsible for subsurface porosity defects are nitrogen and hydrogen.

There is a definite distinction between "porosity defects" and "blows." Porosity defects are "chemical in nature" and result when liquid metal becomes supersaturated with dissolved gases during melting or pouring. The ensuing discontinuities are present as discreet voids that may be rounded or irregularly shaped in the solidified casting and generally lie just under the casting surface. Conversely, "blows" or "blowholes" are a physical or mechanical problem related to the inability of decomposed core and mold gases to escape from the mold cavity, either through permeability or venting.[14]

The appearance of the subsurface porosity defects resulting from the preceding sources may take numerous shapes but usually form as either small, spherical holes (sometimes elongated or pear- shaped) and called pinholes, or larger, irregularly rounded holes or irregularly shaped fissure type defects.[1,8,13,15,16] The internal surfaces of the resultant holes may be 1) oxidized, 2) lined with a shiny graphite film, or 3) contain slag or manganese sulfide inclusions·[1, 5, 8]

Although the technical literature contains a large amount of work describing porosity defects and the metallurgical practices that promote the occurrence and treatment of such defects, relatively little experimental work had been conducted in the area of chemical binder induced mold-metal interface porosity reactions. Investigations that have been conducted in this area have been generally limited to discussions that potential problems exist when using high nitrogen (urea) furans, and to a lesser extent, shell and oil-alkyd-isocyanate systems. Until 1974, minimal research had been conducted in determining how various core and mold-making parameters affect the incidence of porosity defects with chemical binder systems. This lack of research has continued during the ensuing 25 years.

The phenolic urethane resin system consists of no-bake and gas cured resins**;** both systems consisting of two resin components. Part I is a phenolic resin (poly-benzylic-ether-phenolic resin) diluted approximately 50% by solvents. Part II is a polymeric di-isocyanate resin diluted with approximately 25% solvents. The solvent can be either aliphatic or aromatic in composition. The primary purpose of the solvents is to reduce binder viscosity. Typically, the viscosity's of the Part I and Part II resins are adjusted to 200 cps or lower to provide good pump-ability, rapid and efficient sand coating qualities and good flowability of mixed sand. A second purpose of the solvents is to enhance resin reactivity. An amine-based catalyst is used as the curing agent for the no-bake binder while a gaseous amine (triethylamine or dimethylethyl amine) is used for the gas-cured binder.

Although the general chemistry of phenolic urethane binders remains essentially the same as the system investigated in 1974, there have been numerous changes in current resin formulations involving the solvent system as well as base phenolic resin system. The Part I phenolic resin has been modified to reduce odor by reduction in the level of free formaldehyde, and this becomes especially apparent when hot foundry sands are used. In addition, because of efforts to reduce solvent evaporation into the atmosphere, the solvent system has been modified extensively to incorporate higher boiling point solvents or new solvents systems having improved environmental properties.

Being organic based systems, the phenolic-urethane family of binders are composed of only four basic elements: carbon, hydrogen, nitrogen and oxygen as shown below:

Approximate Composition of Phenolic Urethane Binders

% Carbon	% Hydrogen	% Nitrogen	% Oxygen
72.0	8.5	3.9	15.5

With phenolic urethane systems, the nitrogen component is associated solely with the polyphenyl polyisocyanate (Part II) binder component. Part I, or the hydroxyl containing phenolic binder component, contains no nitrogen. Elements of concern to the foundryman need be limited to only nitrogen and hydrogen**;** carbon and oxygen from the binder usually present no problem because the high silicon content of gray iron acts to suppress the formation of carbon monoxide porosity. For comparison purposes, hydrogen and nitrogen contents of other popular resin binder systems are listed below:

	% Nitrogen	% Hydrogen [1]	% H2O
No- Bake Oil	1.76	7.0	none
Low N_2 Furan	1.20	6.0	4.0
Med N_2 Furan	4.5	6.0	15.0%

1.) Associated with Organic Components

Each of the preceding elements, including moisture, may react or combine in numerous ways to provide the necessary conditions that favor porosity formation. The following gaseous reactions are thermodynamically possible and under the right conditions may occur at the mold-metal interface:

Binder ----------- > H (nascent) -> H_2 (g)

Binder ----------- > N (nascent) ---> N_2 (g)

Fe + H_2O vapor (binder) --------> FeO + 2H (nascent)

3 H_2 (binder) + N_2 (binder) > $2NH_3$(g) --------> 6H(nascent) + 2N(nascent)

FeO + C (binder) ---------> CO (g) + Fe

While the first four reactions are likely to provide both surface and subsurface porosity defects, the last reaction usually results only in surface defects, such as pockmarking or more frequently, lustrous carbon laps and surface wrinkles[17]. When an organic binder thermally degrades, hydrogen and nitrogen are liberated in the nascent or atomic form. In this mono-atomic state, they are readily soluble in molten iron, and if present, dissolve quite easily in both molten gray and ductile irons. If ammonia forms, it also may dissociate into both nascent hydrogen and nitrogen. Since the solubility of hydrogen and nitrogen in liquid iron is far greater than in solid iron, these gases will precipitate out of solution as gas bubbles during solidification if they are present in amounts greater than the solid solubility limits. The shapes of the resulting gas holes may vary from small, widely dispersed spherical shaped holes lying just under the surface to numerous fissure type holes, often resembling shrinkage defects and are usually perpendicular to the casting surface. In either case, absorption of nitrogen and \ or hydrogen by the molten iron, either individually or jointly, may result in subsurface porosity defects.

Clearly, many factors are involved in the development of binder-associated defects; neither they nor the various coremaking parameters and foundry melting variables that have a direct influence on the occurrence of such defects were well understood in 1974. Recognizing this situation, the object of the original research investigation was aimed at determining how such variables influence the occurrence of porosity defects. In addition, the development of remedial techniques to alleviate these problems were also extensively studied.

Experimental Procedure

The experimental program used in this investigation was divided into two phases. The first phase was devoted to 1) the development of a suitable test having the capability to produce porosity defects and 2) the delineation of core making and metal processing variables having an effect on porosity generation. The cylindrical test casting shown in Figures 2 and 3 was developed for these tests to observe the extent of porosity formation under various test conditions. This "stepped cone" configuration was selected because its design was such that core decomposition gases would be generated rapidly while the casting was still in the molten state. In addition, this design easily lent itself to the study of section size, re-entrant angle (hot spot) and other geometric effects.

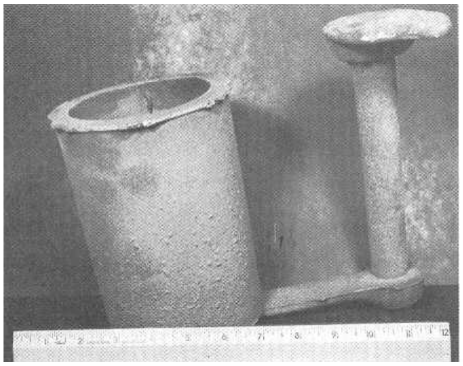


Figure 2: Cylindrical test casting illustrating gating system employed.

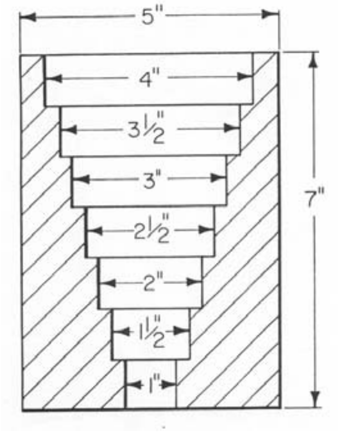


Figure 3: Dimensions of cylindrical test casting.

The majority of molds used for the production of test castings were made with a zero nitrogen no-bake furan binder. The base core sand mix used for most of the experimental work consisted of the phenolic urethane no-bake binder (PUN) mixed with a high purity, washed and dried, round grained, silica (W/D) sand. The coremaking procedure used throughout most of this work consisted of adding the phenolic polyol resin component (Part I) and the catalyst to the sand and mixing for two minutes, followed by the addition of the polyisocyanate component (Part II) and mixing for an additional two minutes. The mix was immediately hand rammed into the core box and the stepped cone cores were stripped within five minutes.

Gray and ductile irons of the compositions shown in Table 1 were utilized in the investigation, although the bulk of the experimental work was conducted with a high carbon equivalent iron (4.3 C.E) inoculated with standard foundry grade (0.75% minimum calcium) ferrosilicon in the ladle. Inoculant addition levels were 0.25% silicon, based on the pouring weight.

Table 1: Compositions of Test Castings Poured

	High C.E.	**Low C.E.**	**Ductile**
% C	3.50	2.90	3.5 – 3.6
% Si	2.40	1.70	2.5 - 2.6
% Mn	0.50	0.50	0.35
% S	0.02	0.02	0.01 max
% P	0.02	0.02	0.01
% Mg	---	---	0.04
% Ni	---	---	0.80

All heats were prepared with virgin charge materials to insure low initial gas content and were poured at selected temperatures as measured with a Pt-Pt 10% Rd immersion pyrometer and a high speed, strip chart recorder. Variables studied during this phase of the investigation included binder ratio, binder level, pouring temperature, sand type and permeability, mixing effects, metal composition and core age. Within each series of tests, the conditions were controlled as carefully as possible and individual variables altered to determine their effect on porosity.

The second phase of the experimental work was devoted to developing remedial techniques to prevent porosity. To a great extent, this effort was very dependent upon the first phase of the work in that conditions that were found to promote porosity were used exclusively. Therefore, it was a prerequisite to develop the capability to produce binder-associated gas defects at will. The same melting and coremaking procedures previously described were likewise used at this time. Techniques studied in attempt to eliminate defects included 1.) investigation of various grades of iron oxide, 2.) ladle additions of ferrotitanium, as well as titanium and zirconium based ferroalloy inoculants, 3.) use of core sand additives, 4.) core baking, and lastly, 5.) a study of experimental core coatings. During this phase of the work, variables found responsible for porosity formation were held constant during the preparation of test castings.

The extent of porosity formation in all castings was determined by careful sectioning at several locations. To determine whether any metallurgical changes resulting from porosity formation had occurred, metallographic investigations of the cast structure in the mold-metal interface area were also carried out. To observe the nature of the internal surfaces of gas porosity defects, a scanning electron microscope was utilized.

Results

Parameters Affecting Formation of Binder Related Porosity Defects: It is of great importance to the foundryman to fully understand the nature of and fundamental chemistry of no-bake binder systems in order to assure their correct usage. This is particularly true with phenolic urethane no-bake (PUN) systems. In general, any one of a number of minor operating variables can exert a cumulative effect on the performance of no-bake binders. Some of these factors which contribute to binder misuse are: 1) infrequent calibration of binder pumps and sand flow rates on continuous mixers, 2) general equipment malfunctions related to binder pumps, worn mixer auger screws or blades, poor housekeeping practice, etc, 3) intentional unbalancing of binder components to facilitate stripping, or 4) general misunderstanding of possible potential consequences resulting from any of the preceding. To determine how these effects and other variables may affect porosity formation, numerous experimental heats were poured to study their effect on casting integrity.

Effect of Binder Part I to Part II ratio. The effect of the ratio of Part I to Part II resin components for PUN binders on porosity propensity is shown in Table 2.

Table 2: Effect of Binder Ratio on Porosity Formation

Binder Level (pct)	**Ratio Part I to Part II**	**Porosity Extent**
1.5 (1998 version)	60 : 40	Nil
1.5	60 : 40	Nil
1.5	50 : 50	Nil to Trace
1.5	40 : 60	Traces to Moderately Severe
1.5 (1998 version)	35 : 65	Severe
1.5	35 : 65	Severe
Test Conditions: PUN binder on a Washed and Dried silica sand, Iron Chemistry – 4.3 C.E. Gray Iron Pouring Temperature – 2700^{o}F, PUN Binder lot manufactured in 1998		

The tabulated results are a summary of numerous casting tests conducted at various stages during the investigation and are somewhat dependent or related to a number of other variables to be discussed in subsequent sections of this paper. The results designated with the comment "1998 version" refer to casting tests performed on current resin formulations.

Binder ratios of 60:40 (Part I : Part II) provided sound test castings in every case under the test conditions used. As this ratio became balanced (50:50), trace amounts of porosity were found in a few test castings but the majority of test castings made with balanced ratios were sound. In those cases where porosity was found, a substantial portion was as surface porosity or semi-rounded holes (pockmarking). As the binder ratio was unbalanced again in favor of excess Part II (40:60 and 35:65), greater amounts of subsurface porosity formed in the test casting. The types of defects observed and described as varying in intensity from nil to very severe are shown in Figure 4.

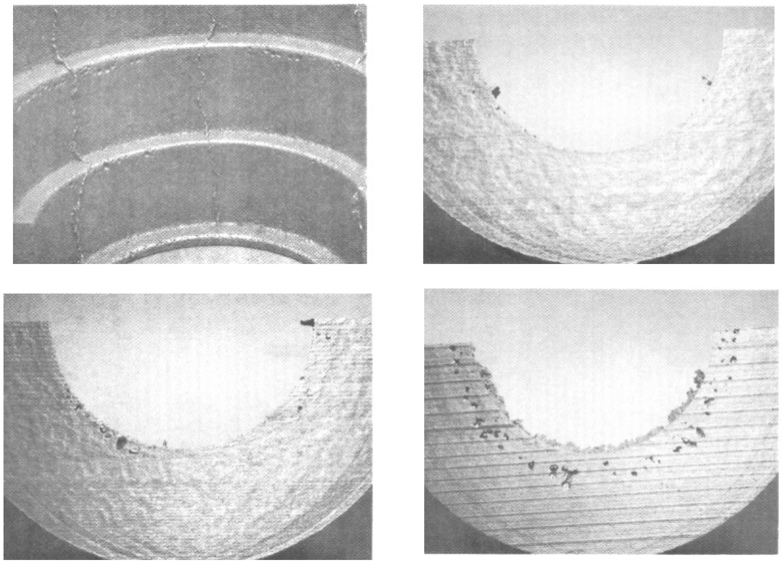


Figure 4: Types of porosity defects encountered in test castings.

Although the recommended ratio for running PUN binders varies between a 55:45 to 60:40 ratio, in actual practice, extreme ratios favoring excess Part II or polyisocyanate are often encountered. Such problems often arise from worn or defective binder pumps, air in binder lines, changes in binder viscosity from temperature, inefficient mixing, and numerous other less incidental, but often overlooked sources. For example, in the early 1970's, it was not unusual to foundries to run binder ratios favoring excess polyisocyanates to facilitate the stripping of difficult cores or to increase fully cured core strengths.

New resin formulations (1998 versions) showed very little difference in casting performance compared to 1974 versions. Binder ratios in which unbalanced ratios of 60:40 were employed produced sound castings. Unbalanced binder ratios favoring excess Part II or the isocyanate component once again were very susceptible to severe subsurface porosity.

Effect of Binder Level: To determine the effect of binder level on porosity susceptibility, test castings were poured with test cores made with binder levels ranging from 1.25 percent to an extreme of 3.0 percent. At some of these levels, the ratio of Pt I: Pt II was again varied to determine effect on porosity formation. (It should also be noted that although these higher levels may never be encountered in actual practice, they were intentionally selected to magnify the effect of binder level or the effect of reclaimed sands having high "LOI" values.) The results obtained from these tests showed that as the binder level increased at the same Pt I : Pt II ratio, the severity of the porosity defects likewise increased. At the highest binder level tested, porosity tended to form at even balanced ratios as shown in Table 3.

Table 3: Effect of Binder Level on Porosity Formation

Binder Level (pct)	Ratio Pt. I : Pt II	Porosity Extent
3.0	60 : 40	Nil to Trace
3.0	50 : 50	Moderate
3.0	40 : 60	Severe
3.0	35 : 65	Very Severe
1.8	60 : 40	None
1.8	50 : 50	Trace
1.8	35 : 65	Severe
1.5	60 : 40	None
1.5	50 : 50	None to Trace
1.5	35 : 65	Severe
1.25	50 : 50	None
1.25	35 : 65	Moderate
Test Conditions: PUN on W/D silica sand, 4.3 C.E. Gray Iron Part I : Part II ratio varied, Pouring Temperature – 2700^{o}F		

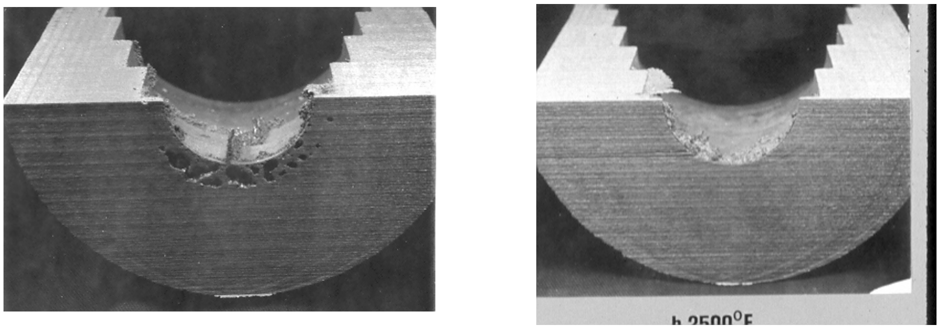
These results show that if sufficient amounts of evolved hydrogen and / or nitrogen decomposition gases are made available to the solidifying irons, porosity will generally occur even with favorable binder ratios and using relatively high pouring temperatures. This same phenomena can be extrapolated to include what the consequences will be when using reclaimed core or molding sands having high loss on ignition values. Excessive amounts of dissolved gases stemming from inappropriate charge materials or liquid metal processing will likewise be more susceptible to core gas defects from absorption of hydrogen and / or nitrogen.

Effect of Casting Temperature -- Although the previously reported results have shown significant effects of both binder ratio and level on porosity formation, their effect was very temperature dependent. Results obtained from test castings poured at several casting temperatures and incorporating unbalanced binder component ratios favoring excess Part II are shown in Table 4.

Table 4: Effect of Pouring Temperature on Porosity Formation

Binder Level (pct)	Pouring Temperature	Porosity Extent
1.5	2780	Very severe – gross with some traces of fissures
1.5	2700	Severe
1.5	2625	Traces
1.5	2550	None
3.0	2700	Very Severe
3.0	2600	Moderate
3.0	2500	None
Test Conditions: PUN on W/D silica sand, 4.3 C.E. Gray Iron Part I : Part II ratio held constant at 35 to 65		

These results demonstrate the temperature dependency of porosity formation with PUN binders. Pouring temperatures of 2700^{o}F and higher (as measured in the pouring ladle) produce severe subsurface defects when unbalanced ratios are used. Such pronounced behavior is not observed when these ratios are balanced or when excess Part I is used. Reducing the pouring temperature at both binder levels resulted in lesser amounts of porosity until at the lowest temperature sound castings were achieved. A comparison between sectioned test castings poured at 2700^{o}F versus 2500^{o}F and made with 3.0% total binder is shown in Figure 5.



a. 2700°F *b. 2500°F*

Figure 5: Effect of pouring temperature on porosity formation

Pouring temperature effects were further demonstrated by pouring experimental test step cores that were coated with the polyisocyanate binder component (Part II). For these tests, pouring temperatures of 2500°F were employed and test cores were bonded with an unbalanced (35:65 ratio) binder system containing 3.0% total resin. Sectioned test castings obtained under these conditions were entirely sound.

The porosity-temperature dependency can best be illustrated in Figure 6.

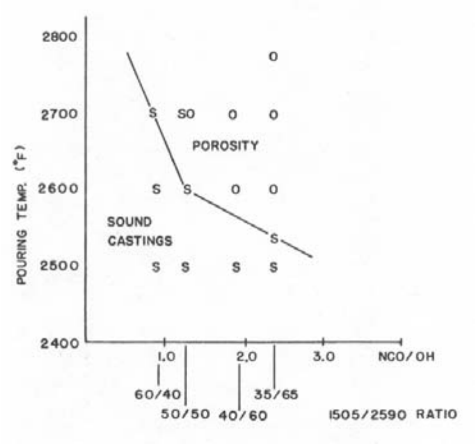


Figure 6: Effect of pouring temperature and binder ratio on porosity formation

In this figure, pouring temperature is plotted against binder ratio. It is interesting to note that there appears to be a definite region in which porosity seems to form and also another definite region where sound castings are obtained. In between these two areas, porosity may or may not occur depending on other liquid metal processing factors. Similar findings on the effect of pouring temperature with other binder systems have been reported by other investigators.[4, 16]

Effect of Section Size: In those castings containing porosity, it occurred in preferential locations. Deep seated, subsurface porosity was usually located adjacent to the 90° re-entrant angle or "step" and most often occurred in section thickness' ranging between 7/8 inch and 1-3/8 inch. These locations act as localized hot spots since a small volume of the core is heated from both sides by the solidifying iron. In thinner sections, varying degrees of surface porosity or pockmarking were often found. From the appearance of these defects, it appears probable that they were formed late in the solidification process by gaseous decomposition products pushing away the semi-skinned over casting surface.[17] Since these bubbles are formed late in the solidification process at the mold-metal interface, not enough time was available for their dissolution. Consequently, a depression is left in the surface when final solidification commences. The extent of this surface porosity varied between somewhat large, semi-rounded holes extending at most only 1/8 inch into the surface to very small surface pores having no appreciable depth.

Sand Effects -- The type of sand used in experimental test cores had a significant effect on porosity formation. Some results obtained with a typical lake sand and a washed and dried silica sand are listed in Table 5.

Table 5: Effect of Sand on the Formation of Porosity

Sand Type	Binder Level (pct)	Ratio Pt. I to Pt. II	Porosity Extent
W/D Silica	1.5%	35 : 65	Severe
Lake Sand	1.5%	35 : 65	Severe
Test Conditions: 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F W/D – Washed and dried Silica sand, 4.3 C.E. Gray Iron Part I : Part II ratio held constant at 35 to 65			

Although several castings were poured under identical conditions and also from the same ladle, severe subsurface porosity was very prevalent with washed and dried silica sand while castings made with the Michigan Lake sand were entirely sound. The behavior of lake sand in eliminating gas defects may possibly be attributed to either its significantly larger quantity of surface impurities, bulk impurities or greater permeability.

To determine the effect of surface purity on influencing gas porosity, an acid treatment was administered to the lake sand to remove trace surface impurities. The acid treatment consisted of soaking the sand in a 10 percent solution of sulfuric acid for 24 hours followed by a 24-hour water wash and drying. Such treatments have been shown to be very effective in removing these impurities.[18]

Comparisons of casting results obtained with acid-treated versus untreated Lake Sands are shown in Table 6.

Table 6: Effect of Acid Surface Treatments on Porosity Susceptibility

Sand Treatment	Binder Level (pct)	Ratio Pt. I to Pt. II	Porosity Extent
None	1.5%	35 : 65	None, totally sound
Acid Treated	1.5%	35 : 65	None, totally sound
Test Conditions: 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F Lake Sand, 4.3 C.E. Gray Iron			

The results in Table 6 showed that removal of surface impurities by acid leaching was not effective in promoting porosity and no porosity was observed in the test castings .

Because of the known effect of permeability on porosity defects and the potential chemical effect of sand type, several other sands having a wide range of compositions, permeability's and AFS grain fineness distributions were selected for testing. These tests were run to determine relative porosity susceptibilities of common core and molding sands. The results of casting tests all run under identical conditions along with the physical properties and resultant porosity sensitivities are summarized in Tables 7 and 8.

Table 7: Effect of Sand Type on Porosity Formation

Sand Treatment	Binder Level (pct)	Ratio Pt. I to Pt. II	Porosity Extent
Silica Sand No. 1	1.5%	35 : 65	Severe
Silica Sand No. 2	1.5%	35 : 65	Severe
Silica Sand No. 3	1.5%	35 : 65	Severe
Silica Sand No. 4	1.5%	35 : 65	Trace to Moderate
Sand No. 5	1.5%	35 : 65	None, totally sound
Lake Sand	1.5%	35 : 65	None, totally sound
Test Conditions: PUN Binders applied to above sands, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F			

Table 8: Physical and Chemical Properties of Sands

Sand	% SiO_2	% Fe_2O_3	% Al_2O_3	GFN	Permeability	Porosity Sensitivity
Silica Sand No. 1	99.88	0.02	0.10	67	95	High
Silica Sand No. 1	99.88	0.02	0.10	37	225	High
Silica Sand No. 1	99.88	0.02	0.10	131	20	High
Silica Sand No. 1	99.6	0.018	0.27	54	180	Moderate
Sand No. 5	99.2	0.13	0.40	55	190	None
Lake Sand	94.8	0.44	2.12	56	150	None

Based on the preceding, even though the sands tested had a wide range of AFS grain fineness and permeability's, there doesn't appear to be any correlation between these parameters and porosity sensitivity. The trend in Tables 7 and 8 is such that the lower the impurity level, and particularly the iron oxide content of the sand, the greater the sensitivity of the system for promotion of porosity defects. Hence, although very pure, round-grained sands offer outstanding core and mold making properties, they may not produce the best castings, as less impure sands seem to do.

The intentional addition of impurities such as iron oxide to sand mixes is widely recognized as an effective means of controlling porosity, veining, improving hot strength and other less incidental properties. However, the presence of such a small amount of iron oxide as a bulk impurity associated with the sand mineralogy appears to have a significant effect on retarding or inhibiting porosity formation. In addition, the type and purity of iron oxide will be shown to have an overriding effect on porosity formation.

Binder Dispersion or Mixing Effects -- Proper dispersion of the liquid binder components on sand surfaces is a necessary prerequisite in the production of high quality cores and molds. Mixers which were prevalent in the early to mid 1970's often provided relatively poor blending of binders and subsequent coating of sand grain surfaces. This was especially true of slow speed screw or auger types, which left something to be desired where high mixing efficiency is desired. Also, if the screw blades or paddles and trough are not cleaned regularly to remove resin buildup, are poorly designed or wide clearances exist due to wear, then poor mixing action will result. If proper dispersion of the binder components is not realized, many areas of the core surface will essentially contain varying ratios of binder components even though the bulk core may contain the proper total amount of each component. Although high speed, high efficiency sand mixers along with advanced resin metering systems, often with computerized controls, have been developed in the 1990's and have resulted in dramatically improved mixing, consideration must still be given to properly maintaining the equipment.

To determine the effect of proper binder dispersion on mixing efficiency, several core mixes were made in a laboratory high intensity batch mixer and mixed for various times to simulate mixing conditions ranging from very poor to excellent. Experimental test cores made using mixing times of 5, 10, 20, 30 and 60 seconds for each component (double for actual total mix cycle) are shown in Figure 7.

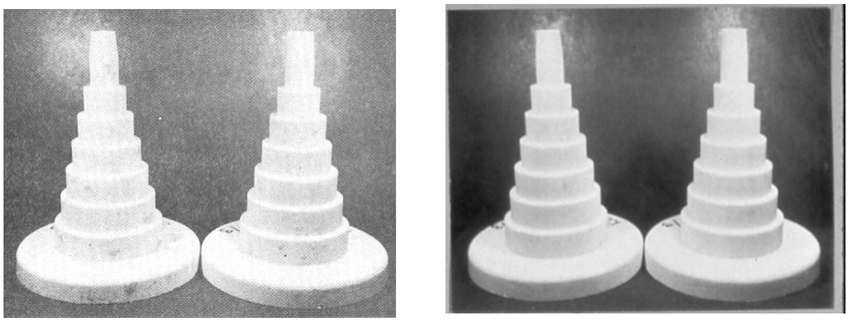


***Figure 7: Effect of mixing time on binder dispersion*.**

All of these cores were prepared with balanced ratios of Pt. I : Pt. II (50 : 50) on the standard washed and dried silica sand. Cores prepared with total mixing times of 10, 20 and 30 seconds exhibited pronounced non-uniform binder dispersion and were spotty in appearance. This was found to be most pronounced with the 10 and 20 second mix cycles. Longer mixing times of 80, 120, and 240 seconds provided very uniform results. Physical properties such as scratch and tensile strengths of mixes mixed for total times of 40 seconds and longer were not impaired even though traces of inadequate mixing were apparent on the 40-second mix.

The results obtained from casting tests using test cores prepared in the described manner are listed in Table 9.

Table 9: Effect of Mixing Time and Mixing Efficiency on Porosity Formation

Mixing Time per component (seconds)	Total Mixing Time (seconds)	Binder Level	Ratio Pt. I to Pt. II	Porosity Extent
5	10	1.5%	50 : 50	Very Severe
10	20	1.5%	50 : 50	Moderate
20	40	1.5%	50 : 50	Nil to Moderate
30	60	1.5%	50 : 50	Nil to Traces
40	80	1.5%	50 : 50	Nil to Traces
60	120	1.5%	50 : 50	None, totally sound
120	240	1.5%	50 : 50	None, totally sound
Test Conditions: PUN Binders applied to above sands, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F				

To briefly summarize these results, short mix cycles of 10 to 40 seconds total time tended to promote the formation of both surface and subsurface porosity. Only trace amounts of subsurface porosity, probably better described as microporosity, were found in the remaining castings made with cores mixed for intermediate times of 60 to 80 seconds total. In castings containing pronounced defects, these defects were obviously formed where the solidifying casting was in contact with binder-rich areas and particularly those containing excess polyisocyanate. Sound castings were obtained when total mixing times ranged from 2 to 4 minutes.

Effect of Metal Composition -- The type and composition of the castings poured had a significant effect on porosity formation. Results of these tests are shown in Table 10.

Table 10: Effect of Type and Composition of Castings on Porosity Formation

Low Carbon Equivalent Iron (3.40 C.E. - Class 50)			
Binder Level (pct)	**Ratio Pt. I to Pt. II**	**Pouring Temperature**	**Porosity Extent**
1.5%	60 : 40	2700	Subsurface microporosity, small fissures
1.5%	60 : 40	2500	Nil amounts
1.5%	50 : 50	2700	Small fissures, subsurface holes
1.5%	50 : 50	2500	None, totally sound
1.5%	40 : 60	2700	Severe fissures and severe subsurface porosity
1.5%	40 : 60	2500	None, totally sound
Test Conditions: PUN Binders on Washed & Dried Silica Sands, 3.4 C.E. Gray Iron, Pouring Temperature – varied between 2500°F and 2700°F			

Table 11: Effect of Type and Composition of Castings on Porosity Formation

High Carbon Equivalent Iron (4.3 C.E. - Class 20)			
Binder Level (pct)	**Ratio Pt. I to Pt. II**	**Pouring Temperature**	**Porosity Extent**
1.5%	60 : 40	2700	None
1.5%	60 : 40	2500	None
1.5%	50 : 50	2700	Nil to Trace
1.5%	50 : 50	2500	None
1.5%	40 : 60	2700	Trace to Moderate
1.5%	40 : 60	2500	None, totally sound
Test Conditions: PUN Binders on Washed & Dried Silica Sands, 4.3 C.E. Gray Iron, Pouring Temperature – varied between 2500°F and 2700°F			

Table 12: Effect of Type and Composition of Castings on Porosity Formation

Ductile Iron (60 – 40 – 20)			
Binder Level (pct)	**Ratio Pt. I to Pt. II**	**Pouring Temperature**	**Porosity Extent**
1.5%	35 : 65	2700	None, Totally Sound
1.5%	35 : 65	2500	None, Totally Sound
1.5%	35 : 65	2700	None, Totally Sound
1.5%	35 : 65	2500	None, Totally Sound
1.5%	35 : 65	2700	Nil to Trace
1.5%	35 : 65	2500	None, Totally Sound
Test Conditions: PUN Binders on Washed & Dried Silica Sands, 60-40-20 Ductile Iron Pouring Temperature – varied between 2500°F and 2700°F			

The porosity forming tendencies seemed to be greatest for the low carbon equivalent iron and least for ductile iron. Porosity defects in all gray iron castings formed readily when unbalanced binder ratios favoring excess polyisocyanate were employed. Porosity defects that formed in low carbon equivalent irons were predominantly fissure type defects, although some rounded and irregularly shaped holes also formed. Ductile iron castings seemed to be far less susceptible to defect formation than either composition of gray iron. Results obtained with a high carbon equivalent iron as used throughout this investigation have been previously reported and remain unchanged.

Although it is commonly accepted [1,19] that ductile iron is more susceptible to porosity defects, the present investigation tends to show just the opposite. However, most of these previous findings or observations have been with ductile irons containing appreciable amounts of aluminum and poured in green sand molds.[8,15] It is also generally held that ductile irons are more prone to hydrogen defects arising from interactions with water vapor and magnesium. This is probably related to the fact that the residual magnesium is influencing hydrogen solubility [15,20,21] or is assisting the reduction of water vapor. However, Dawson and Smith also showed that although high residual magnesium contents increased hydrogen solubility in ductile iron castings poured in green sand molds, pinholes still did not form.[20] Since the chemistry and gaseous thermal decomposition products for PUN binders are obviously more complex than those interactions with green sand molds, the performance of ductile iron with these binders may in actuality differ considerably. However, one would expect porosity formation in ductile irons to be much more difficult due to the higher melt interfacial surface energy. Other investigators have also reported a relationship between porosity and surface tension in ductile irons.[9,22,23] Lastly, the bubbling of magnesium vapor through the metal during the nodularizing process effectively purges most dissolved gases from the metal, allowing for possible absorption of core gases without supersaturation.[23, 24]

Effect of Core Age -- The effect of test core age within the first 24 hours after strip had no effect on porosity formation. Test castings poured with cores used immediately after strip or after overnight aging performed in a similar manner. Results obtained from aging tests poured at three pouring temperatures are listed in Table 13.

Table 13: Effect of Core Aging on Porosity Formation

Core Age (hours)	Binder Level	Ratio Pt. I to Pt. II	Porosity Extent	Pouring Temperature (°F)
1	1.5%	35 : 65	Very Severe	2700
24	1.5%	35 : 65	Moderate	2700
1	1.5%	35 : 65	Nil to Moderate	2600
24	1.5%	35 : 65	Nil to Traces	2600
1	1.5%	35 : 65	Nil to Traces	2500
24	1.5%	35 : 65	None, totally sound	2500
Test Conditions: PUN Binders applied to Washed and Dried Silica, 4.3 C.E. Gray Iron, Pouring Temperature – varied between 2700°F and 2500 °F				

If test cores made with unbalanced systems were aged over several days under ambient conditions, the severity of the defects increased slightly. This phenomenon appears to be related to moisture from atmospheric humidity combining with unreacted NCO groups in the polyisocyanate and forming urea structures.[25,26] The porosity forming tendencies of this latter group of substances is well known.[1,2,8] They are reported to readily break down into ammonia derivatives at high temperatures that later dissociate into nascent hydrogen and nitrogen,[1,27] both of which are highly soluble and dissolve very readily in molten irons.

Elimination of Porosity Defects

Numerous methods, both metallurgical and chemical, were investigated as potential remedial techniques to eliminate defects in castings poured under somewhat adverse conditions. Most of these techniques were straightforward in approach**;** however, those techniques that may have resulted in reduced melt quality, such as trace element additions of tellurium, selenium or bismuth, were not examined in the original research work since it was felt that these methods would not be very feasible. Any potential gains in porosity elimination may have been overshadowed by chilling and/or poor metal quality. New techniques incorporating the use of proprietary inoculants containing carefully controlled additions of surface active elements as well as elements that neutralize nitrogen (by forming stable nitride compounds) were examined and are reported herein.

Effect of Titanium and Zirconium Additions -- Additions of titanium have long been recognized as helpful additives in reducing subsurface porosity defects related to nitrogen.[1,3] To determine if such additions were effective in controlling porosity in test castings poured with PUN test cores, varying levels of 70% ferrotitanium (20 mesh x down) were added in the ladle prior to pouring. Besides using 70% FeTi, two commercial gray iron inoculants containing titanium were also examined. The effect of zirconium on porosity reduction was evaluated by adding 0.05% zirconium as ferrosilicon zirconium as well as incorporating zirconium into a high potency proprietary inoculant. The casting results obtained from these tests are listed in Table 14.

Table 14: Effect of Titanium and Zirconium Additions on Porosity Formation

% Addition	Binder Level (pct)	Ratio Pt. I to Pt. II	Porosity Extent
None	1.5%	35 : 65	Very Severe
0.025% Ti as FeTi	1.5%	35 : 65	Trace to Moderate
0.50% Ti as FeTi	1.5%	35 : 65	None, totally sound
0.025% Ti as Inoc. A	1.5%	35 : 65	Trace
0.030% Ti as Inoc. A	1.5%	35 : 65	None, totally sound
0.030% Ti as Inoc. B	1.5%	35 : 65	None, totally sound
0.050% Zr as FeSiZr	1.5%	35 : 65	None, totally sound
0.025% Zr as Inoc. C	1.5%	35 : 65	Trace to None
Test Conditions: PUN Binders applied to Washed and Dried Silica sand, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F Inoculant A - **52% Si, 11% Ti, 1.25% Ca, 1.0% Al, Bal - Fe** **Inoculant B - 75% Si, 11% Ti, 5.5% Ba, 3.5% Mn, 1.25% Ca, 1.0% Al, Bal - Fe** **FeSiZr - 35% Si, 33% Zr, 2.5% Ca, 1.0% Al, Bal - Fe**			

In almost all cases, the addition of small amounts of titanium as a ladle addition was effective in eliminating subsurface porosity in castings made with cores bonded with excessive Part II polyisocyanate levels. In the case of 70% ferrotitanium additions, titanium additions of 0.05% were effective in removing subsurface porosity defects, a considerable amount of surface porosity or small pores remained.

Since it is well known that 70% ferrotitanium may be difficult to dissolve at temperatures below 2,700°F, resulting in erratic recoveries and results, two proprietary titanium containing gray iron inoculants were also investigated. Proprietary Inoculant A was effective in eliminating porosity when the titanium addition level was 0.03%. Inoculant B is based on 75% ferrosilicon, and since inoculants based on 75% FeSi dissolve more rapidly than those based on 50% FeSi [28], Inoculant B appeared to be more effective at somewhat lower titanium addition rates.[29] No porosity was found when titanium addition levels of 0.025% were employed with Inoculant B. Ferrosilicon zirconium was almost as effective in eliminating porosity but somewhat higher levels of 0.05% zirconium had to be added. This was not unexpected because of the higher atomic weight of zirconium. Inoculant C is a potent proprietary gray and ductile iron inoculant[30] containing 30 to 33% oxy-sulfide forming elements that was modified by the addition of 9.0% zirconium (in the form of ferrosilicon zirconium). With zirconium additions of 0.025%, trace to no subsurface porosity was found. Since zirconium forms much more stable nitrides than titanium, more zirconium must be added because of its higher atomic weight. Hence, it is likely that higher levels of zirconium need to be added to Inoculant C for complete porosity elimination. Although Inoculant C did not entirely eliminate porosity, it was the most effective of the three inoculants tested in reducing chill and produced the most uniform microstructure, consisting of 100% Type A graphite flakes.

Metallographic inspection of the castings made with 70% ferrotitanium showed that higher addition rates of titanium (0.05% and greater) were effective in tying up nitrogen as titanium compounds (TICN or TiN) and preventing re-precipitation as gas holes during solidification. Similar results were observed with the proprietary inoculants. The ferrotitanium additions were not, however, effective in preventing surface reactions associated with lustrous carbon pockmarking reactions from the high pouring temperatures employed during this phase of the investigation. The proprietary inoculants also showed some signs of lustrous carbon related surface porosity.

Effect of Zirconium and Selenium Inmold Additions – Small additions of selenium to stainless steel castings poured in green sand molds are very effective in eliminating porosity.[31] Selenium is a surface active element and can result in degenerate graphite forms. To evaluate the effect of controlled amounts of zirconium and selenium on porosity elimination in gray iron, very small amounts were added (8.0% zirconium as FeSiZr) to a proprietary 9 gram inmold inoculating tablet. A second experiment was also run with a supplemental addition of 3.3% selenium to a 8.0% zirconium modified proprietary inmold inoculating tablet. The casting results obtained from these tests are listed in Table 15.

Table 15: Effect of Selenium and Zirconium Additions on Porosity Formation

% Addition	Binder Level (pct)	Ratio Pt. I to Pt. II	Porosity Extent
None – Standard 75% FeSi	1.5%	35 : 65	Very Severe
Inoculant Tablet D 0.0048% Zr	1.5%	35 : 65	Severe
Inoculant Tablet E 0.0048% Zr and 0.0019% Se	1.5%	35 : 65	Severe
Test Conditions: PUN Binders applied to Washed and Dried Silica sand, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F Standard Inoculant - Foundry grade 75% FeSi with 0.75% Calcium, 0.33% addition rate **Inoculant D - 9 gram inoculant tablet containing 27.7% Si, 28.41 oxy-sulfide forming elements plus 8.0%Zr, Bal - Fe** **Inoculant E - 9 gram inoculant tablet containing 25.6% Si, 26.88% oxy-sulfide forming elements plus 8.0%Zr and 3.3% Se, Bal - Fe** **Zirconium and Selenium percentage levels based on the 35 lb. step cone pouring weight**			

Castings made with either zirconium by itself or with both selenium and zirconium contained subsurface porosity. The presence of porosity in the above castings is probably the result of addition of insufficient treatment alloy. It is interesting to note that the microstructures of both castings treated with the 9 gram inoculating tablets were somewhat improved, containing 100% Type A graphite, compared to the standard ladle inoculation with 75% foundry grade ferrosilicon containing 0.75% calcium, which contained some Type B and D graphite. Additional experimental work remains to be conducted in this area using larger inserts with greater amounts of zirconium and selenium additions.

Effect of Iron Oxide Additions -- The addition of even small amounts of red iron oxide had an overwhelming effect on porosity elimination. The results of additions of varying amounts of 200 mesh red iron oxide (Fe_2O_3 or hematite) to PUN core sand mixes are shown in Table 16.

Table 16: Effect of Red Iron Oxide (Hematite) on Porosity Formation

Binder Level (pct)	Ratio Pt. I to Pt. II	% Red Iron Oxide	Porosity Extent
1.5%	35 : 65	0 – None	Very Severe
1.5%	35 : 65	0.025	Trace to Moderate
1.5%	35 : 65	0.05	None, totally sound
1.5%	35 : 65	1.50	Trace
1.5%	35 : 65	2.0	None, totally sound
1.5%	35 : 65	3.0	None, totally sound
Test Conditions: PUN Binders applied to Washed and Dried Silica sand, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F			

Additions of as little as 0.25% red (hematite) iron oxide were sufficient to inhibit the formation of all traces of porosity in test castings poured under adverse testing conditions. It must be noted that since commercial foundry grades of red iron oxide occur naturally, not all grades may work like the grades used in the experiments. Further, it has been shown that additions of Fe_3O_4 (magnetite) are not nearly as effective as hematite in controlled casting tests.[32,33] Casting tests run comparing hematite to magnetite are shown in Table 17.

Table 17: Effect of Iron Oxide Type on Porosity Formation

Binder Level	% Iron Oxide	Mesh Size	Oxide Type	Porosity Extent
1.5%	0	1.5%	None	Severe
1.5%	0.25	1.5%	Fe_2O_3 **(red)**	None
1.5%	0.25	1.5%	Fe_3O_4 **(black)**	Severe
1.5%	0.25	1.5%	Hematite Ore	Severe
Test Conditions: PUN Binders applied to Washed and Dried Silica, 4.3 C.E. Gray Iron, Pouring Temperature – 2700°F, 35 : 65 Ratio of Part I to Part II Fe_2O_3 assay: 87% Fe_2O_3, 8.0% SiO_2, 2% Al_2O_3, Balance not reported Fe_3O_4 assay: 62% Fe_3O_4, 1.5% SiO_2, 4% Al_2O_3, Balance not reported				

These results clearly show the effects of iron oxide mineralogy and chemistry. Although two of the iron oxides had similar mesh sizes (325 mesh x down), the 325 mesh red iron oxide (hematite) clearly outperformed the black iron oxide (magnetite) as well as a coarser (100 mesh) European hematite ore of relatively high purity. It can be concluded that iron oxide purity doesn't appear to be a determining factor in the performance of an iron oxide and its subsequent effect on porosity elimination. Although black iron oxide additions are commonly in use today, much of the acceptance of black oxides is more likely related to reduced surface area considerations. Sand additives with reduced surface area allow for reduced resin consumption and improved coremaking economics. However, careful consideration must be given to the superior effectiveness of red oxide in preventing porosity when choosing an oxide addition.

It should be noted that although some iron oxides may contain various percentages of TiO_2 (titanium dioxide) in their mineralogy, it is doubtful whether sufficient time or quantities of the element titanium could be reduced and be available to react with nitrogen during the casting process. Hence, the presence of titanium dioxide in iron oxide would not impart any beneficial effect on minimizing porosity susceptibility of nitrogen bearing resins. All of these findings illustrate that red iron oxide almost always outperforms black iron oxide in producing sound, porosity free castings as well as minimizing other resin related defects such as lustrous carbon.[34]

To determine the effect of iron oxide granularity, other grades of hematite (Fe_2O_3) were tested using the conditions outlined in Table 17. At 1.5% and 4.00% levels, a much coarser grained hematite addition was also was effective in eliminating defects even though it was relatively randomly distributed in the core due to its large particle size. This behavior, coupled with how effective 0.25% red iron oxide was in eliminating porosity, appears to preclude the long accepted role of iron oxide in preventing defects. The role of iron oxide in preventing porosity has long been linked with its ability to react with silica to form fayalite which in turn forms a "physical" barrier preventing gas solution. At the low levels investigated and because of the behavior of the coarse grained hematite, it appears probable that iron oxide is somehow affecting the kinetics of gas absorption by the solidifying metal. Regardless, such small additions could certainly not be effective barrier formers at the levels employed.

To further establish if the formation of a slag-type barrier at the mold-metal interface is a viable mechanism responsible for porosity elimination, additions of sodium fluoroaluminate (or cyrolite) were employed as sand additives. Cryolite has a melting point of 1,825^{o}F and does not rely on reacting with silica as does iron oxide to form a slag**;** cryolite will liquify in-situ to form such a barrier. Additions of 0.5%, 1.0% and 2.0% were evaluated in exactly the same manner as the previously reported iron oxide additions. The results obtained from these tests are shown in Table 16.

Table 18: Results of Casting Tests with Cryolite Additions

Binder Level (pct)	**Ratio Pt. I to Pt. II**	**% Cryolite**	**Porosity Extent**
1.5%	35 : 65	0 – None	Severe
1.5%	35 : 65	0.5	Severe
1.5%	35 : 65	1.0	Severe
1.5%	35 : 65	2.0	Severe
Test Conditions: PUN Binders applied to Washed and Dried Silica sand, 4.3 C.E. Gray Iron, Pouring Temperature – 2700^{o}F			

In these castings, veining defects were minimized but considerable burn-on was present which appeared to be the result of severe sand fluxing. However, in all cases, severe subsurface porosity was found in the test castings.

Core Washes -- A considerable number of experimental core washes were applied to test cores to determine effectiveness as porosity inhibitors. Most of the washes were proprietary formulations but contained varying amounts of red iron oxide. Others were made by incorporating additives to a base gel. Casting tests were run using those conditions previously described that promoted porosity. Results of these tests indicated that proprietary red iron oxide (Fe_2O_3) bearing washes provided very slight or no reduction in porosity defects. Experimental washes composed of aluminum powder and titanium powder provided similar performance. However, a 100% red iron oxide (Fe_2O_3) wash, and another prepared with sodium silicate and iron oxide (Fe_2O_3) completely prevented the formation of porosity. This achievement was accomplished but at the expense of severe surface finish degradation. The sodium silicate red iron oxide wash deteriorated the casting surface only slightly but the 100% red iron oxide wash had a very deleterious effect on the surface. Overall results tended to indicate that adequate amounts of iron oxide were not employed in proprietary washes; however, in experimental washes with red iron oxide, too much was added with a resultant loss in surface smoothness. Apparently, a delicate balance exists between the amount of iron oxide needed for porosity elimination compared to the amount that results in deteriorated surface finish.

Core Post-Baking -- To determine the effect of core baking on porosity elimination, several test cores were subjected to post-baking or curing for three different times. The results of these tests are summarized in Table 19.

Table 19: Results of Casting Tests with Test Cores baked for 1, 2, and 4 hours

Binder Level	**Ratio Pt. I to Pt. II**	**Temperature (^{o}F)**	**Time (hours)**	**Porosity Extent**
1.5%	35 : 65	450	1.0	Severe
1.5%	35 : 65	450	2.0	Nil to Trace
1.5%	35 : 65	450	4.0	None
Test Conditions: PUN Binders applied to Washed and Dried Silica, 4.3 C.E. Gray Iron, Pouring Temperature – 2700^{o}F				

Castings made with test cores baked at 450°F but for only one hour contained severe porosity defects. Intermediate times of 2 hours significantly reduced the extent of porosity. Baking for 4 hours at 450 °F produced a distinctive core color change to chocolate brown and had a significant effect on porosity elimination. For thorough baking to occur, it has been found that a color change usually accompanies such a treatment and up to 55% of the binder is volatilized. Although such lengthy times may be impractical, higher baking temperatures or short times at high temperatures might be effective in reducing overall binder level in the core surface layers. Baking also demonstrates that some free hydrocarbons are undoubtedly volatilized and nitrogen components from the Part II resin may undergo further reactions to form more stable compounds.

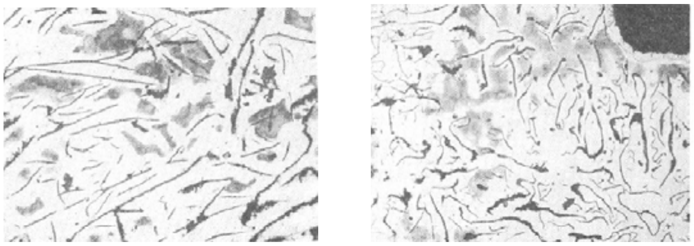
DISCUSSION

Although several variables have been identified that either exaggerate or promote the formation of porosity defects in PUN binders, these variables are in one way or another related to the gaseous decomposition products generated by the resin during casting. Decomposition gases consisting of both hydrogen and nitrogen are readily liberated during casting pouring and during subsequent solidification. High pouring temperatures further enhance both the breakdown rate and amount as well as favor increased gas solubility in the liquid metal. High pouring temperatures also have a significant effect on liquid metal surface tension, which has been shown to have a significant effect on porosity formation.[9,11] Because both hydrogen and nitrogen are readily available and extremely soluble at the casting temperatures employed, their effect on potential porosity defects is often additive.

Numerous chemical analyses taken during this investigation showed that considerable pickup of both hydrogen and nitrogen occurred in the immediate subsurface layers when conditions favoring porosity were employed. At depths of 0.25 in. and more below the cored surface, hydrogen and nitrogen levels tended to be quite low and representative of the base metal. It is probable that just before solidification, momentary supersaturation of both hydrogen and nitrogen exist just under the casting surface. This complex nitrogen/hydrogen effect has long been recognized by other investigators.[6,27,35] Further, if a considerable amount of nascent nitrogen is dissolved in a casting from unbalanced binder ratios favoring excessive polyisocyanate components, the presence of even a small amount of hydrogen will serve to lower the overall solubility of nitrogen. Stated another way, hydrogen may be exerting a catalytic effect on nitrogen to enhance porosity formation.

The same effect of alloying elements on gas solubility is well known and acts in a similar manner. To further aggravate conditions, if the melt initially has a high gas content resulting from the use of poor charge metallics or carbon additives,[36] then the tolerance for additional solution of nascent mold or core gases is reduced considerably and porosity formation becomes extremely favorable.

Typical microstructures exhibited by sound and porosity containing castings taken in the immediate vicinity of the mold-metal interface are shown in Figure 8.

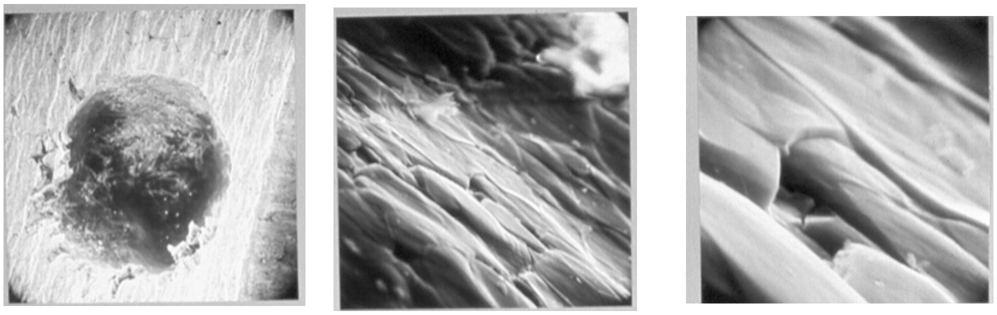


a. Sound ***b. porosity containing***

Figure 8: Microstructures of (a) sound and (b) porosity containing test castings immediately below mold-metal interface (100x magnification).

In all cases, no differences in either matrix structure or graphite morphology were found. Both microstructures contained the same ferritic type matrix with Type A graphite. The solidification rate and composition of all base gray iron heats favored this type of structure. Although it is widely recognized that hydrogen and nitrogen are carbide stabilizers and favor formation of pearlite as well as alter graphite structure,[37-41] it appears that insufficient time was available during solidification and subsequent cooling through the transformation temperatures, for such phases to form.

Although most gas holes exhibited a bright or shiny interior of a graphitic nature, no such films were observed during optical metallography. Further examination of these areas with a scanning electron microscope showed distinct layers of what appears to be a crystalline graphitic coating lining the interior of the gas holes (see Figure 9). The presence of this crystalline film has been reported by numerous other investigators.[1,8]



a. 20 x *b. 2000 x* *c. 5000x*

Figure 9: Scanning electron micrographs taken from interior of porosity defects (a - 20x, b - 2000x and c - 5000x magnifications).

The morphology of gas holes that formed took many shapes, even in the same casting. Both fissure type gas holes as well as small spherical and pear shaped holes were very often observed in the same casting. Although for the most part, gas holes that formed were located just underneath the surface, and most extended no more than 0.25 in. into the casting, a few castings contained gas fissures almost 0.50 in. long (Figure 10).

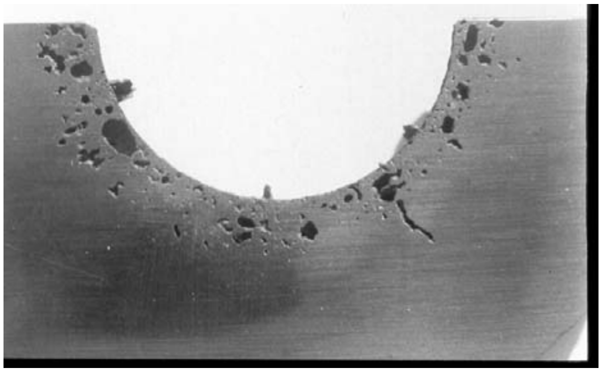


Figure 10: Morphology of subsurface gas porosity (1.5x magnification).

Because of the sub-surface nature of the defects, the incorporation of large amounts of alloying elements that form stable nitrogen compounds may not be needed since only these sub-surface layers are affected. Incorporation of proprietary nitrogen stabilizing elements or "scavengers," which include both titanium and zirconium based ferroalloys, may offer additional possibilities for treating binder induced porosity defects. Likewise, inmold inoculating tablets incorporating zirconium for nitrogen control and small amounts of selenium for hydrogen control also offer promise for defect elimination.

Although the porosity studies focused on using ladle additions of nitrogen stabilizing ferroalloys, the use of beneficiated ilminite ore has also been shown to be a very effective method of introducing the element titanium. Mikelonis[42] reported that ilmenite ore was the most cost effective method of introducing 0.04 to 0.07 percent titanium levels to cupola melted irons. The ilmenite was added as 3 in. x 2 in. ilmenite ore to the cupola charge. In this research, it was reported that titanium recovery levels were 30 to 40 percent of the total amount of titanium in the ore. Other developments aimed at improving titanium recoveries are based on using beneficiated ilmenite ore that incorporate a proprietary blend of halide containing fluxes.[43] Such products are available in the form of a briquette or tablet and can be used either as a furnace addition or ladle addition. These products may also provide improved melt quality by coalescing liquid and / or solid slags with the mild fluxing agents incorporated in the tablet or briquette.

It is not well understood how small amounts of red iron oxide (0.25% addition rates) were so effective in eliminating subsurface porosity in the test castings. It has been suggested that the red iron oxide is exerting some type of "catalytic effect" on binder decomposition products that minimize or alter the generation of nitrogen and hydrogen gases. One such theory is that when exposed to the sudden high temperatures of iron casting, red iron oxide (Fe_2O_3) readily releases oxygen. This released oxygen immediately reacts with nitrogen decomposition products from the binder to form stable NO_x compounds [44]. Since hematite (red iron oxide) has a much higher concentration of oxygen compared to magnetite (black iron oxide), and based on the improved performance of red iron oxide compared to black, this mechanism certainly appears to be very feasible. However, it is recommended that additional research be conducted in this area.

CONCLUSIONS

1.) Unbalanced PUN systems favoring excess Part II or polyisocyanates promote the occurrence of gaseous mold-metal reactions resulting in both surface and subsurface gas defects. High binder levels also tended to slightly increase defect propensity even when balanced ratios were employed. Balanced or slightly unbalanced isocyanate / polyol hydroxyl ratios favoring excess Part I were relatively unsusceptible to such defects although a few cases of slight porosity were found.

2.) Inadequate mixing that results in poor distribution of the binder components in the mix was also found to accentuate porosity formation.

3. The temperature of the molten iron as it contacted the core surface was found to have a significant effect on porosity formation when castings were poured under conditions favoring their formation. Severe porosity defects were formed at 2700°F and higher. As the temperature was reduced, these defects became fewer in number and intensity until none formed at 2550°F.

4. Porosity formation was found to be very sensitive to core sand type. Lake sands were relatively insensitive to defect formation while high purity, round grained white silica sands were found to be very sensitive.

5. Cast iron composition had an effect on porosity formation. Ductile iron was least susceptible to defect formation while low carbon equivalent irons were most susceptible.

6. Addition of titanium compounds, either in the form of 70% ferrotitanium or proprietary gray iron inoculants containing titanium were effective in eliminating porosity defects. Zirconium additions were also somewhat effective in eliminating defects at the addition levels employed. Incorporation of ferrosilicon zirconium into a proprietary inoculant was also found to reduce the incidence of defects.

7. The addition of small amounts of red iron (Fe_2O_3) oxide (82% minimum purity) to silica sand mixes was extremely effective in eliminating porosity. Sound castings were obtained with additions as small as 0.25% red iron oxide. Black iron oxides were not anywhere as effective as red iron oxide.

8. No metallurgical changes in either graphite morphology or matrix structure occurred in the gas affected mold-metal interface region. A layer or film, probably graphitic in nature, was found lining the internal surfaces of most gas holes.

9. Porosity defects tended to form in geometric hot spots or re-entrant angles on the test casting. The location seems to indicate that localized heating of the core re-entrant angles creates a condition that results in a momentary supersaturation of the surface layers. Gas analysis taken well beneath the affected surface layers showed normal gas contents.

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