COLD SETTING STUDIES OF FOUNDRY SANDS BONDED WITH FURAN RESINS

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Abstract. Cold setting characteristics of furan resins were studied on a laboratory scale by treating with phosphoric acid. Resins incorporating various sugars were prepared and their setting characteristics studied. It was found that the amount of acid required for maximum strength was critical. Addition of water to the system enhanced the rise in strength of the binder. Resins containing hexose, produced a very strong bond and the rise in strength was rapid.

Experiments to study the curing mechanism of the resins indicated the possibility that at low levels of catalyst addition, the acid and the resin formed concentric films around the sand grains and the curing of the resin occurred by diffusion of hydrogen ions through an interface between the films.

The cold setting process for making sand moulds and cores based on furan resins was developed in the early 1960's and has since gained popularity resulting in its extensive use all over the world. This process employs the exothermic chemical reaction of an organic resin with a mineral acid. The hardening and curing of sand takes place in intimate contact with the pattern or the corebox. This enables the pattern or the corebox to be stripped after the bond has developed. The likelihood of sagging or distortion is thus eliminated. Very large cores of high dimensional accuracy can be prepared by this process.

Furan resins are formed by the partial polymerisation of urea–formaldehyde/phenol–formaldehyde with furfuryl alcohol. These resins set and cure without the application of heat when treated with a mineral acid. With increasing acid addition a better cure is obtained as the cure is inversely proportional to the pH value within certain limits.[1]

Epstien,[2] Parkes[3] and Cutter and Finley[4] have reported that about 30–50%*phosphoric acid was necessary for complete setting of resins (based on urea–formaldehyde). However, Kumar et al.[5] have observed that the acid addition of 2.5–7.5% was necessary for the complete setting of the resin. They have attributed this decrease in the acid requirement to the higher sand temperature, which ranged from 30 to 35° during their study.

It follows from the observations made by Kumar et al.[5] that variations in the acid could be critical to the setting properties of the furan sands.

The present investigation was undertaken to examine critically the no-bake process for core and mould making, in order to make the process amenable for tropical climates. The effects of water addition to the system was also studied as the kinetics of the reaction between the acid and resin is influenced by the dilution and cooling effect of water. As water is very well tolerated by the resins based on urea–formaldehyde,[2] only this category of resins was selected.

Sugars are known to influence the thorough-setting properties of the resin-bonded sands. Resins containing sucrose, hexose and molasses respectively were prepared and their setting properties studied by treating them with phosphoric acid. The following tests were carried out and the conditions of testing have been set out in Tables 1 and 2.

(1) Setting of resins without sand to study the reaction mechanism between the resin and acid catalyst.

(2) Setting of resins containing various sugars with sand to establish the effect of sugars on the speed of strength development and thorough-setting properties of sands.

Materials

Sand

Chemical Composition. L/I 1.14%, SiO_2 97.42%, Al_2O_3 1.15%, Fe_2O_3 0.17%, CaO 0.12% and TiO_2 traces

Sieve Analysis

Sieve aperture (mm)			Sand retained(%)
—2.0	+	1.6	0.13
—1.6	+	1.0	0.54
—1.0	+	0.4	5.43
—0.4	+	0.315	5.71
—0.315	+	0.20	45.31
—0.20	+	0.16	18.83
—0.16	+	0.10	10.78
—0.10	+	0.071	4.31
—0.063	+	0.071	1.50
Pan	—	0.063	3.62
Afs clay grade†			3.84

Binders

1. Urea–formaldeyhde–furfuryl alcohol, 72% solids.

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* UF urea formaldehyde, FA furfuryl alcohol, S sugars, M molasses, H hexoses, P phosphoric acid (per cent by weight of resin).

† Mainly silt, an active clay, as determined by methylene blue test, was less than 0.1%.

TABLE 1. SETTING OF RESIN WITH SAND AT 35–40°.

Resin	Amount of H_3PO_4 (% by wt of resin)	Tensile strength (KN/m²) of test specimen broken after					
		2 hr	4 hr	8 hr	12 hr	16 hr	24 hr
UF–FA 3% by wt of sand	3	85	140	345	725	1070	1105
	4	275	345	725	1105	1280	1290
	5	310	415	795	1210	1310	1343
	6	165	310	585	865	930	930
UF–FA–M 3% by weight of sand	7·5	—	275	930	1070	1105	1105
	10	—	105	1000	1140	1210	1210
	12·5	—	175	830	1000	1070	1175
UF–FA–S 3% by wt of sand	3	105	175	415	830	900	900
	4	175	345	725	1105	1175	1175
	5	345	555	930	1380	1555	1590
	6	450	620	900	1210	1310	1310
UF–FA–H 3% by wt of sand	5	70	450	1140	1175	1175	1175
	6	175	1070	1380	1450	1485	1520
	7	310	1380	1690	1690	1690	1690
	9	650	1450	1935	1970	1970	1970
	10	690	1655	1830	1795	1760	1655

Tensile tests were performed on a Riddsdale sand strength testing machine. The original values were in psi but these were converted to kilo Newtons per square meter(KN/m²) by using the following factor:

$$psi = \frac{(454/10^3)kg}{(2.54/10^2)\,m\,(2.54/10^2)m}$$

$$= \frac{(454/10^2)}{(2.54/10^2)(2.54/10^2)} \times \frac{9.81}{10^3} = 6.903\ KN/m^2$$

TABLE 2. SETTING OF RESIN WITH SAND AT 35–40° (Effect of addittion of water on the rise in strength)

Resin	Amount of water added (% by wt of resin)	Tensile strength (KN/m²) of test specimen broken after					
		2 hr	4 hr	8 hr	12 hr	16 hr	24 hr
UF–FA for 5% acid	10	105	555	1280	1380	1450	1450
	20	35	415	1380	1760	1760	1760
	30	—	655	1725	1865	1900	1900
	40	—	105	1380	1760	1830	1830
UF–FA–M for 10% acid	0	105	345	900	1140	1175	1210
	10	310	830	1485	1465	1450	1450
	20	245	620	1415	1380	1380	1345
UF–FA–S for 5% acid	10	245	655	1175	1555	1590	1590
	20	105	555	1280	1625	1725	1725
	30	35	555	1590	1830	1865	1865
	40	—	690	1725	1935	2000	2000
UF–FA–H for 7% acid	10	865	1690	2070	2210	2210	2210

2. Urea–formaldeyhde–furfuryl alcohol modified with sucrose, 75% solids.

3. Urea–formaldehyde–furfuryl alcohol modified with molasses, 74% solids.

4. Urea–formaldehyde–furfuryl alcohol modified with glucose, 75% solids.

Acid. Phosphoric acid s.g. 1.7 (85%) commercial.

Methods

Setting Without Sand

Setting without sand experiments were carried out as follows: 0.01 ml phosphoric acid was placed on a glass plate and 0.2 ml resin was placed over the acid drop. Another drop of resin was placed beside the acid resin drop for comparison. Time required for hardening the top surface of each drop was noted. Other changes observed during the setting of these drops were recorded and are presented in Table 3.

Setting With Sand

Speed of strength development of resin bonded sand was determined as rise in tensile strength of standard test pieces (25.4 × 25.4 mm cross-section area) with respect to time. For this purpose sand and acid were first mixed together, in a batch mixer, for one minute, followed by the addition of resin and mixing for another minute. Two batches of sand were prepared for each composition and six test-specimens (in all 12 specimens) prepared from each batch. Temperature was maintained by placing the sand and the specimens in an oven. Two tensile strength tests were performed at the same time at regular intervals after ramming the test pieces. The first and second tests were carried out after intervals of 2 and 4 hr respectivley while subsequent tests were performed at 4-hr interval, missing the test after 20 hr. The conditions of the tests have been set out in Tables 1 and 2 and the rise in tensile strength graphically represented in Figs. 2–10 by plotting the tensile strength along the ordinate and the time along the abcissa.

TABLE 3. SETTING OF RESINS WITHOUT SAND AT 35–40°.

| Resin	Hardening time (hr)	Changes accompanying the hardening of resin	Condition of resin after 24 hr
UF–FA	3	Resin drop had granular shape, colour brown	Completely set greenish brown
UF–FA–S	3½	Resin spreads slightly, colour brown	Completely set, brown
UF–FA–M	2	Resin spreads slightly, colour dark brown	Completly set, dark brown
UF–DA–H	1	Resin spreads to thin film, colour green	Completely set, green
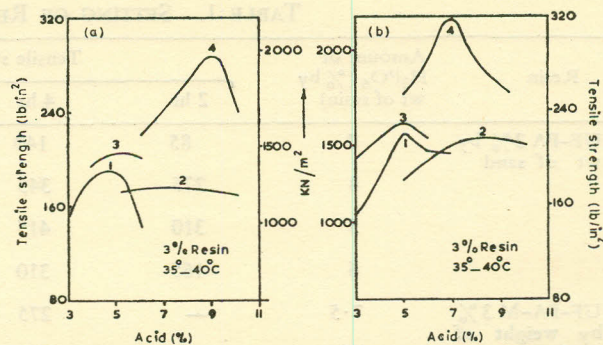
Fig. 1 (a). Effect of varying acid on maximum tensile strength of specimens bonded with different resins, (b) effect of varying acid on miximum tensile strength of specimens bonded with different resins diluted with H$_2$O (10% by wt of resin). (1. UF–FA, 2. UF–FA–M, 3. UF–FA–S, 4. UF–FA–H).
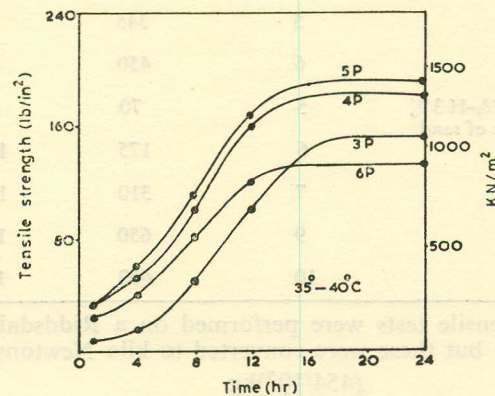

Fig. 2. Effect of varying acid on rise in tensile strength of specimens bonded with 3% UF–FA.
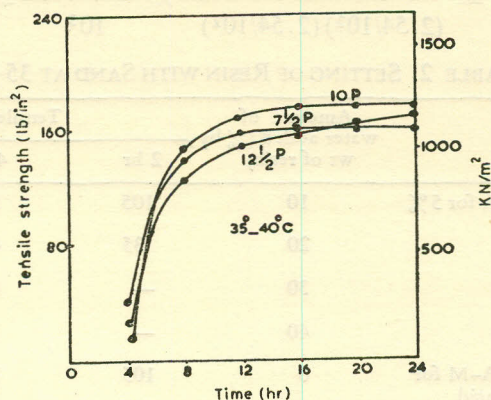

Fig. 3 Effect of varying acid on rise in tensile strength of specimens bonded with 3% UF–FA–M.

Results and Discussion

Setting Without Sand

Results of experiments for setting of resins without sand have been presented in Table 3. All the four resins were hard after ½–3½ hr and apparently the reaction proceeded till the resin was completely set. Resin-containing hexose tended to flow on the
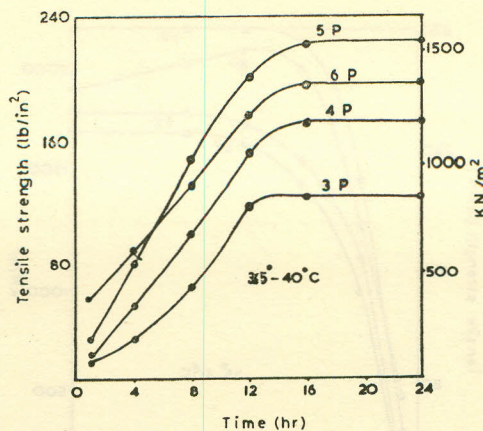
Fig. 4. Effect of varying acid on rise in tensile strength of specimens bonded with 3% UF–FA–S.
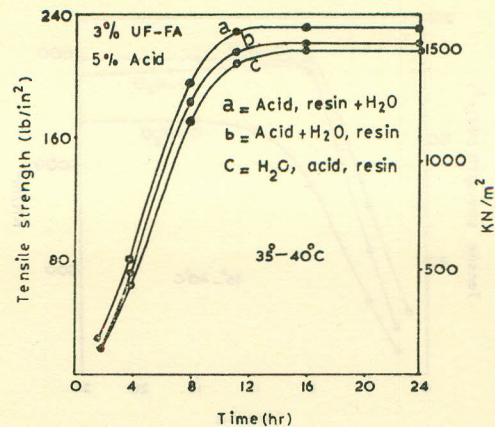

Fig. 6. Effect of order of mixing H_2O, acid and resin on rise in tensile strength.
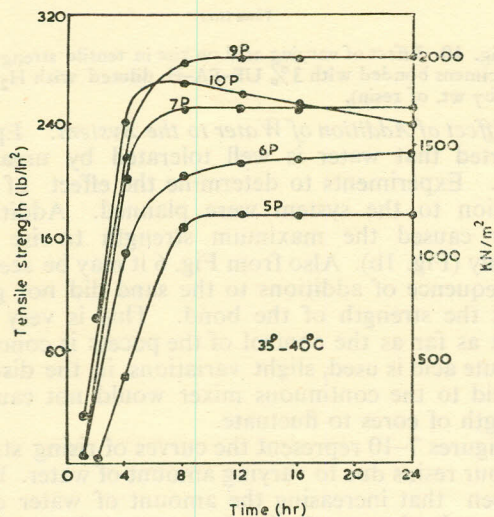

Fig. 5. Effect of varying acid on rise in strength of specimens bonded with 3% UF–FA–H.
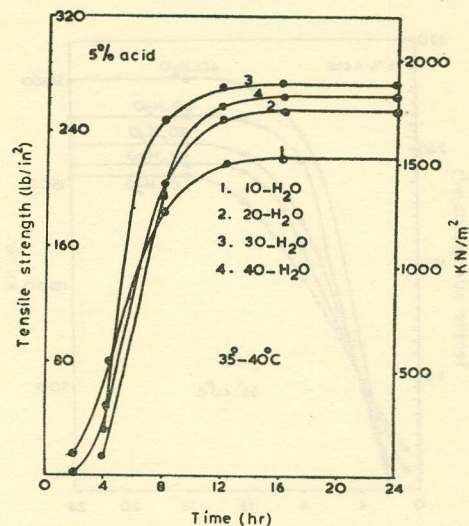

Fig. 7. Effect of adding H_2O (% by wt. of resin) on rise in tensile strength of specimens bonded with 3% UF–FA.

glass plate as soon as the reaction started. This tendency to flow was less for resins containing sucrose and molasses. The sugar-free resin did not flow at all. Resin drops placed on an acid-free glass surface remained liquid even after 24 hr. Results of these experiments show that setting of resin with acid involved a diffusion controlled reaction.

Setting with Sand

Effect of Varying the Acid on the Maximum Strength of Binder. Figure 1(a) indicates the effects of variation in the acid on the maximum tensile strength of the specimens after 24 hr. All the four resins registered an increase in the maximum strength, with increasing phosphoric acid till a peak value for maximum strength was obtained. After that further increase in acid caused the maximum tensile strength to fall. Plain urea–foramldehyde–furfury alcohol resin and those containing sucrose and hexose were very sensitive to variations in the amount of acid but the resin modified with molasses was much less sensitive.

Resin containing molasses produced the weakest

bond, possibly due to the usual impurities present in molasses. The resin containing hexose was the strongest of all the resins (T.S. 1990 KN/m^2).

Effect of Varying the Acid on the Rise in Strength of Binder. The curves showing rising strength due to variation in the amount of acid are presented in Figs. 2–5. For all the four resins, the speed of strength development increased with increasing amount of catalyst. In all these experiments optimum of acid was required for maximum rise in strength of the bond. Further increase in acid lowered both the speed of strength development and the maximum strength.

Rise in strength of plain urea–formaldehyde–furfuryl alcohol was very slow in the first 4 hr. During the next 8 hr the speed of strenght development increased considerably. The resin continued to harden in the next 4 hr but the speed decreased again. After that no further rise in strength occurred, indicating that the resin was completely set (in 16 hr).

The same pattern was observed for the setting of resin containing sucrose. However, this resin was stronger and the rise in strength was slightly faster but this was also a slow setting resin (at 30–40°) as compared to resins suitable for furan sand process.
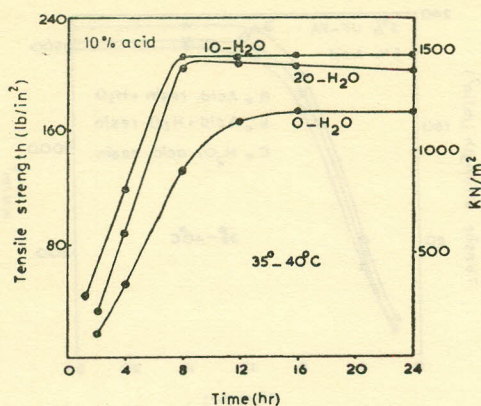
Fig. 8. Effect of adding water (% by wt. of resin) on rise in tensile strength of specimens bonded with 3% UF–FA–M.
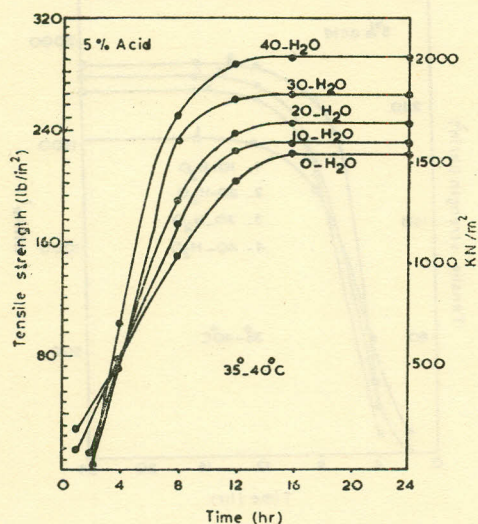

Fig. 9. Effect of adding water (% by wt. of resin) on rise in tensile strength of specimens bonded with 3% UF–FA–S.

Fig. 10. Effect of varying acid on rise in tensile strength of specimens bonded with 3% UF–FA–H diluted with H_2O (10% by wt. of resin).

Resin containing molasses set at a fast rate in first 8 hr but the rise in strength declined considerably in next 4 hr. However, complete setting occurred in 12 hr. The maximum strength was low as compared to the one modified with sugar. Cores made with this resin may be stripped from the core box 4 hr after ramming but the size of cores produced would be limited because of its weak bonding capacity (max. T.S. 1230 KN/m^2).

The resin modified with hexose produced the strongest bond. This can be seen from the curves for rising strength in Fig. 5. The resin was almost completely set in the first 4 hr. Maximum strength obtained by this resin was also very high (T.S. 1990 KN/m^2). Cores made by this resin may be stripped only 1 hr after ramming (as substantial bonding occurs in 1 hr).

It may be noted that both the molasses and hexose-modified resins required more acid for complete setting. This is desirable because, according to Parkes[3] higher acid facilitates core breakdown after casting.
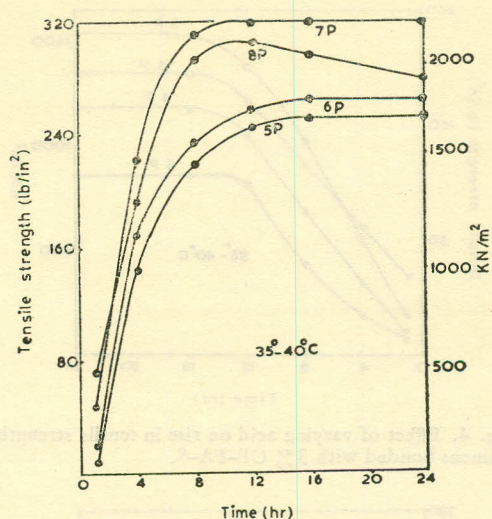
Effect of Addition of Water to the System. Epstien[2] reported that water is well tolerated by urea-based resin. Experiments to determine the effect of water addition to the system were planned. Addition of water caused the maximum strength to rise considerably (Fig. 1b). Also from Fig. 6 it may be seen that the sequence of additions to the sand did not greatly effect the strength of the bond. This is very significant as far as the control of the pocess is concerned. If dilute acid is used, slight variations in the discharge of acid to the continuous mixer would not cause the strength of cores to fluctuate.

Figures 7–10 represent the curves of rising strength for four resins due to varying amount of water. It may be seen that increasing the amount of water caused the speed of strength development to increase considerably. The overall strength of the bond also improved a great deal. Both plain urea–formaldehyde–furfuryl alcohol resin (UF–FA) and that modified with sugar (UF–FA–S), could take up to 30% water (by weight of resin) and the results continued to improve with extra water. Resins modified with molasses and hexose respectively required up to only 10% water (by weight of resins) of maximum improvement in strength.

It is quite possible that addition of water to the system facilitates the diffusion of the $(H_3O)^+$ ions, therefore, better bond is produced. Very large additions of water, i.e. more than 10% would, however, cause problems such as gassed castings and should be avoided. Internal hardness tests were also carried out on cured specimens and it was found that cores bonded with resins containing hexose had hard interiors, and possessed best thorough setting properties. Plain urea–formaldehyde–furfuryl alcohol resins in general produced slightly harder interiors as compared to the resins containing molasses and sucrose.

Comparison of rise in strength curves, for the types of resins (Figs. 2–5), shows that hexose-modified resins set at much faster rate as compared to the other three resins. The 9% acid curve for rise in strength (UF–FA–H) given in Fig. 5 shows that the tensile

strength of the standard specimen was 655 KN/m² after 2 hr and 1450 KN/m² after 4 hr and finally reaching 1965 KN/m² after 24 hr indicating development of more than 70% bond in the first 4 hr. A similar evaluation (speed of strength development of other resins shows that the time for 70% bond development was 6, 9 and 10 hr respectivley for UF–FA–M, UF–FA and UF–FA–S. Similarly the curves for rise in strength (Fig. 10), show addition of 10% water (by weight of resin) to UF–FA–H caused considerable improvement in both the speed of strength development and the maximum strength of the standard specimens. The strength after 2 hr was 865 KN/m² and after 24 hr 2210 KN/m². Compared to 9% acid curve in Fig. 5, the 7% acid curve in Fig. 10 shows an improvement of 65 KN/m²/hr (1690 KN/m² in 4 hr with water and 1450 KN/m² without water with the same time interval) rise in speed of strength development and 240 KN/m² in the final strength. A similar comparison of Figs. 7–10 shows that improvement in the binding capacity of hexose-modified resins as a result of dilution with water was substantial as compared to the other three resins. This shows that hexose-modified resins are by far the strongest of all the four resins studied presently.

Excessive addition of water to the sand system can have deleterious effects (gas holes) on the castings produced in moulds/core made from such sand. However, provided the amount of water does not exceed 10% by weight of the resin, the problem of badly gassed castings should not arise. In this connection, it may be added that evaporation rate of water at 35–40° is fairly high and most of water will evaporate before a metal is poured into the moulds. Besides, the phosphoric acid needed for setting furans at high temperature is substantially less, 5–7.5%, as compared to 30–50% acid needed in colder climates. The amount of moisture generated as a result of decomposition of acid is substantial $(2H_3PO_4 \rightarrow 3H_2O + P_2O_5)$, however, this is not known to yield badly blown castings. Therefore, addition of 10% water to sand system, under tropical conditions, should not cause any problem and may be regarded as safe. The ambient temperature in tropical climates range between 30–40°, and the temperature in a foundry is close to 40°. In light of the preceding discussion, it may be concluded that for such environments, the resins modified with hexose show great promise for use in the furan sand process. As their strength will rise to 550–865 KN/m² the first hour, cores made with this resin may be stripped 1 hr after ramming without danger of sagging or breaking and due to the high inherent strength developed by the resin there is no apparent limit to the size of the cores produced with this resin.

Conclusions

(1) At high ambient temperature the amount of catalyst required for complete setting of resins is very critical. Slight variation in the acid causes wide fluctuations in the strength of bond.

(2) Addition of water to the system improves the setting properties of the resin.

(3) Modification of the urea-based furan resin with hexose considerably improvesl the setting properties of the resin. Thorough-setting properties of this resin are very good. One of the principal requirements of the furan sand process is the bonding capacity of the resin, this must be sufficient to withstand deformation at stripping and the final strength must enable the cores to be handled without damage. Present studies have indicated that hexose-modified urea–based furans fulfil this requirement of furan sand process for its adaptation to suit tropical climate.

(4) It is likely that at low levels of acid addition, concentric films of acid and resin form on the sand grains and the setting of the resin occurs by diffusions of hydrogen ions through an interface between the two films.

Future Work

The present studies have yielded resin fulfilling the principal requirment of the furan process, i.e. the strength needed for stripping and handling the cores without damage. However, information about the castings behaviour, i.e. the defect-forming tendency of the various formulations, is needed to be assessed. For this purpose the present studies are being followed up by work on the phenolic furans together with various formulations of the hexose-modified urea-based furans. Beside assessing the bonding capacity of the resins, the investigation will also include studies of the casting characteristics of these resins. In this connection the hot deformation behaviour and decomposition pattern, the amount and rate of gas given off under the influence of heat (at casting temperatures) of the prepared sands, will be studied. To further evaluate the sand formulations for their defect forming tendencies, actual castings will be poured into the moulds made with these sands and quantity of the defects visually examined. The studies will furnish vital information about the setting and the casting behaviour of resin bonded sands and provide guidelines for the ultimate adaptation of the furan sand process in tropical climates. The work is already underway and the results will be published later on.

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