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FUTUR DES MATIERES PLASTIQUES DANS LES CONSTRUCTIONS NEUVES ET DANS LA MAINTENANCE, LA REHABILITATION, LA REPARATION ET LE RENFORCEMENT DES STRUCTURES EXISTANTES

FUTURE FOR PLASTICS IN NEW CONSTRUCTIONS AND IN MAINTENANCE, REHABILITATION REPAIR AND REINFORCEMENT OF EXISTING STRUCTURES

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FURANIC BINDER OF RESIN CONCRETE USABLE IN WET CONDITION

UN LIANT DE FURANE POUR DES BETONS DE RESINE UTILISABLE DANS LES MILIEUX MOUILLES

When using customary, oil-derived organic resins for the manufacture of resin concrete, it is necessary to ensure that the binder has a moisture content of below 1%, otherwise an extreme reduction of strength, prolongation of hardening period and/or complete failure of polymerization chemism occurs. Furanic resins, produced of inexpensive and low energy requiring vegetable recources show a great affinity to moisture, due the presence of OH groups in their molecular structure, which can be used to advantage for the manufacture of high quality resin concretes even in wet conditions /e.g.using wet aggregate/. Optimization on the type and quantity of polymerization initiator and accelerator can achieve even in unfavourable conditions, such as moisture content of as many as 5% of filler weight, low temperature /~5°C/, high relative humidity of environment /~99%RH/, such mechanical properties as can be attained with other contemporary hardener types only, if the moisture content of the filler be below 0.2%, and in current ambient conditions /20°C, ~50%RH/.

Des résines organiques,habituelment derivées du naphte minéral,peuvent contenir moins que 1% de l'humidité afin d'éviter une polymerisation imparfaite et une réduction de la résistence.Les résines furaniques,qui sont fabriquées des sources végétales par des processus et non coûteux et énergétiquement économiques,produient une grande affinité à l'humidité,qui peuve être utilisée avec avantage pour la fabrication des bétons de résine de grande qualité même dans les conditions humides /p.e.avec des agrégats humides/. La système optimisé /i.e. le type et la quantité de d'initiateur et de l'accélérateur/ pent parvenir mme dans le conditions infavorables /teneur en eau à 5% près du poids du remplissage, la température peu élevée~5°C,l'humidité relative ambiante jusqu'à 99%RH/ des propriétés mécaniques comparables avec les autres systémes contemporains sous les conditions rigoureusement presárites /teneu en eau du remplissage < 0,2%,20°C,50%RH/.

Theoretical Background

The ability of furfural /FAL/ and furfuryl alcohol /FOL/ to polymerize has been known since the time of the discovery of these compounds. Under the effect of mineral acid and temperature furfural makes a transition into an infusible and insoluble mass. However, the experiments intended to obtain technically usable materials on the basis of pure furfural were not successful /1/. When the mechanism of the origin of the polymer was investigated, it was found /2/ that one molecule of water per three molecules of furfural was encluded in the process of polycondensation. According to /3-5/ the structure of the originating polymer is anlogous with natural humin and humic acids and the fundamental impulse for the origin of the polymer is the initial acid hydrolysis of the furan circle:

In this way it is possible to explain one type of reactions as well as the origin of one molecule of water only per three FAL molecules in the course of polycondensation. However, both FAL and FOL react also in the manner customary with aldehydes and alcohols. Therefore, in acid environment also the reactions of the following type can be ecpeted /6/:
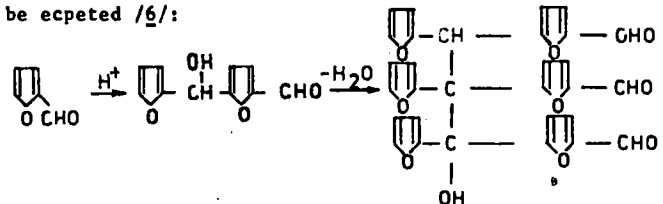
The origin of the polymer on the basis of a FOL of adequate mechanical properties, however, can be obtained by controlled polycondensation only /6/ which gives rise to macromolecules with a relatively low distribution of molecular weights /7/. As a result of the considerable influence of the velocity of the polycondensation reaction on the magnitude of macromolecules /and particularly in the case of a "block" reaction, with the negative influence of the so-called "gel effect"/ it is necessary to preserve the optimum reaction velocity and thus also the sufficiently low distribution of molecular weights and sufficient magnitude of the macromolecules.

The presence of the OH groups in the molecular structure of both FAL and FOL /which is entirely missing from various vinyl monomers/ results in their strong affinity to moisture. This fact can be used, in combination with a suitable type of hardener, for the manufacture of a high quality polymer on the FOL basis even in the presence of considerable moisture content /e.g. wet aggregate in resin
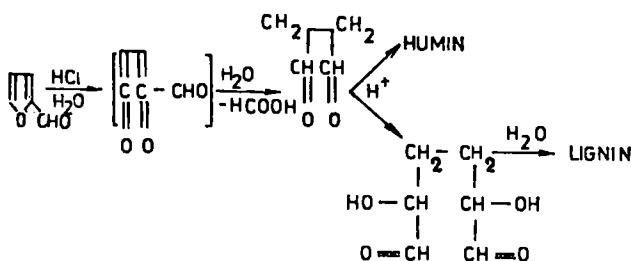
concrete/.

The polycondensation reaction of FOL is a chain reaction dependent on concentration, homogenity and hardener type. For practical purposes /workability/ also the life of the mix is of importance. The use of mineral acids in pure form may ensure that the reaction proceeds until sufficient conversion has been attained /even in wet environment/. However, its velocity may be excessive so that it may be impossible to work the material perfectly because of its short life. A reduction of the concentration of such hardeners, on the other hand, results in insufficient conversion and the necessity of additional thermal treatment. In this respect an acid hardener consisting of 25% of urea nitrate /UN/ and inert silicate filler has proved best so far /8/. Moreover, also an increase of the netting density of the polymer can be expected due to urea, which can be bound into the macromolecules by four functional groups.

The UN $\rightleftharpoons$ HNO_3 + urea dissociation proceeds directly in the reaction system, so that the polycondensation reaction is controlled by the dissociation velocity. The disadvantage of this process consists in the inhibition of polymerization by moisture, which necessitates, for example, the use of a filler with a moisture content inferior to 0.2%. The nagative effect of moisture in this system lies in that the dissociation

$$NH_2 - CO - NH_2 \cdot HNO_3 \rightleftharpoons NH_2 - CO - NH_2 + HNO_3$$
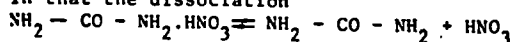
gives rise to the origin of nitric acid which is immeditely dissolved by the moisture present, which reduces its activity. This reduction manifests itself by the reduced mobility of H^+ ions in the reaction environment.

If the polymerization of the FAL-FOL system proceeds in accordance with the scheme

$$\text{monomer} \xrightarrow[k_1]{H} \text{polymer,}$$
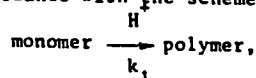
where k_1 is the velocity constant of initiation, it is necessary to ensure that the H^+ ions originated gradually, and only in the mixed mixture, according to the scheme
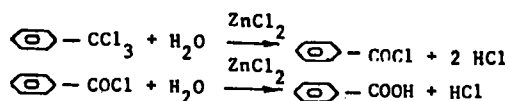
$$\text{hardener} - H \xrightarrow{k_2} \text{hardener} + H^+,$$
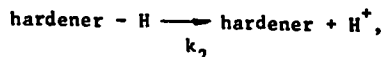
where k_2 is the velocity constant of the origin of the H^+ ions. Optimum properties of the polymer are attained, if both above mentioned processes are in thermodynamic equilibrium.

Accordingly, the requirements imposed on adequate hardener should be met by the materials which are capable of releasing the required acid by their reaction with water. The acid release should proceed slowly and the acid should enable polymerization.

EXPERIMENTAL RESULTS

For polymerization /or the preparation of FOL pre-condensate/ it is possible to use, advantageously, according to /9/ the benzenesulphinic acid, p - toluene-sulphochloride, and α,α,α- trichlorotoluene /TCT/. The polymerization reaction can be accelerated by various water-soluble mineral salts, such as $SnCl_2$, $ZnCl_2$, $AlCl_3$. When TCT is used, in the presence of $ZnCl_2$ as accelerator, the following reaction with water takes place:

$$\langle\text{O}\rangle - CCl_3 + H_2O \xrightarrow{ZnCl_2} \langle\text{O}\rangle - COCl + 2 HCl$$

$$\langle\text{O}\rangle - COCl + H_2O \xrightarrow{ZnCl_2} \langle\text{O}\rangle - COOH + HCl$$

This system will enable polymerization to take place even with a highly diluted monomer /up to 50%/ of sufficient compressive strength /10/. The polymer thus produced will most probably have the character of a foam with microvoids filled with water. The hardening mechanism of this system is explained by that the TCT is soluble in the monomer only, while the $ZnCl_2$ as promoter is soluble in water. The polymerization is initiated on the monomer-water

boundary. The principal disadvantage is the very high polymerization velocity resulting in the impossibility of proper working of the material produced, particularly in a major volume.

According to /10/the resin concrete produced from the FOL with the filler at the ratio of 1 : 6 party by weight, approximately 1,5% of TCT initiator and 60% of $ZnCl_2$ as accelerator /both percentages referring to the weight of the FOL/ with a water contents of 31.4% /by FOL weight/ attains, at a temperature of ~24°C, after an hour a strength only 17.3% lower than wihout water; with a water contents of 48% /by FOL weight/ the reduction is 38.5%. After 3 days the compressive strength was 52.36 MPa without water and 37.4 MPa /i.e. 0.71% of dry strength/ with an admixture of 7.5% of water.

Our experiments /11/ tested particularly the hardeners based on easily available and inexpensive inorganic and organic compounds of chlorine, reacting with water with the origin of HCl, which is particularly suitable because of its high mobility in the mixture. The originating hydrogen chloride is soluble in water in a limited extend and in the reaction environment, even in the presence of H_2O the disociation

$$HCl_{aq} \rightleftharpoons HCl \quad /8/$$
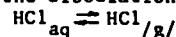
takes place, gaseous HCl can diffuse through the polymerization mixture and initiate polycondensation on a grater scale than it is possible, if non-volatile acids are used.

a/ Systems on the Basis of Phosphorus Chlorides

The raction proceeds according to the folowing schemes:

$$PCl_3 + 3 H_2O \longrightarrow H_3PO_3 + 3 HCl$$

$$PCl_5 + H_2O \longrightarrow 2 HCl + POCl_3$$

$$POCl_3 + 3 H_2O \longrightarrow H_3PO_4 + 3 HCl$$

With these matters the progress of the reaction with water is excessively quick and the process of hardening is sir.. lar with the process using HCl alone. The hardening process cannot be controlled in a way enabling perfect working of the material produced.

b/ Systems on the Basis of Acetyl Chloride /AC/

The assumed reaction is

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$
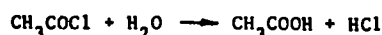
The reaction kinetics of this system with a FOL/FAL = =10/1.5 mixture can be seen in Table 1.

Table 1

FOL+FAL	10	10	10	10	10
CH_3COCl	0.3	0.24	0.15	0.3	0.6
H_2O	-	-	-	0.09	0.09
Time required to attain 40°C /min./	0.5	0.5	1.5	no reaction	3.0

In moisture-free environment the reaction proceeds relatively well. Water retards it. This is due to the fact that both CH_3COOH and HCl are dissolved in water, both compounds having greater affinity to water than the monomer, and the hydrogen chloride originates in insufficient quantity. An increase of AC to over 3%, which would eliminate the negative effect of water, however, is unfeasible for hygienic reasons because of intensive and unpleasant smell.

c/ System on the Basis of Antimony Trichloride

The expected reaction is

$$SbCl_3 + 3 H_2O \longrightarrow Sb /OH/_3 + 3 HCl$$

After mixing $SbCl_3$ with the monomer /at a ratio of 0.1 - -1 : 10 parts by weight/ a speedy reaction and immediate rise of temperature took place in all instances. However, hardening did not take place. The rection took place only at the contact of the monomer with crystals of $SbCl_3$ and

their immediate environment, the remaining monomer not reacting at all. After perfect dispersal in resin concrete composed of 62 parts /by weight/ of 2/4 mm sand, 41.2 parts /by weight/ of 0/0.27 mm sand, 2.4 parts /by weight/ of microfiller /SiO_2/, 10 parts /by weight/ of FOL precondensate, and 1.5 parts /by weight/ of FAL, the results tabulated below /Table 2/ were obtained:

Table 2

Binder+filler /parts by weight/	117.1	117.1	117.1	117.1
$SbCl_3$ /p.b.w./	0.67	0.67	2.0	2.0
Water /p.b.w./	–	6.1	–	6.1
Life /min./	10	17	3	15
Compressive strength /MPa/	41.8	0	37.8	12

The effectiveness of this system with a major moisture content of the filler /~6%/ is low. To ensure higher conversion and, consequently, higher strength heat treatment is necessary.

d/ Systems on the Basis of Benzoyl Chloride /BC/

The compound used /BC/ is an intermediate product of TCT hydrolysis. The reaction proceeded, similarly as in thecase of TCT, according to the scheme:

$$\langle\!\langle\underline{O}\rangle\!\rangle - COCl + H_2O \rightarrow \langle\!\langle\underline{O}\rangle\!\rangle - COOH + HCl$$

The advantage of the BC is apparently the fact that it has a far lower HCl tension than the TCT and, therefore, is more feasible in use for hygienic reasons. The hydrogen chloride, released from the TCT, irritates intensively the mucous membrane even at normal air humidity and excessively accelerates the corrosion of the plant.

The reaction of the BC is considerably slower than that of the TCT /for instance, with 10% of BC per 100% of FOL the hardening takes 5 hours/. The acceleration within a wide range, however, is enabled by the addition of $ZnCl_2$ or $CaCl_2$ without making the progress of polymerization excessively step. Some results for resin concrete of the same composition as in the preceding case are given in Table 3.

Table 3

Binder+Filler /1: 9.18 by weight/ /p.b.w./	117.1	117.1	117.1	117.1	117.1
BC /p.b.w./	0.72	2.4	2.4	2.4	2.4
$ZnCl_2$ /p.b.w./	1.2	1.2	1.0	0.72	1.2
Water /p.b.w./	1.2	1.2	1.2	1.2	2.4
Life /min./	13	3	5	20	15
Compressive strenght after 3 days /MPa/	34.0	36.2	43.3	45.4	36.4

DISCUSSION OF RESULTS AND CONCLUSIONS

A number of experiments have proved that the system of hardening described ad d/ can be used to advantage for furanresin concrete in the presence of high moisture content /Fig.1/. For example, with 25% water contents with regard to FOL /i.e. 2.5% of water with regard to the filler for the given mixture of 1 : 9.18/ it is possible to attain, with 25% of BC and 12.5% of $ZnCl_2$ /with regard to FOL/ a strength of 66% of the value attained without water /with dried filler/ for hardening at a temperature of 24°C for 3 days. Additional curing at temperature increased to 60 – 80°C results in an increased of strength to the value attained with dry filler. With a water contents of 12.5% /with regard to FOL/ and an optimum quantity of 25% of BC and 7% of $ZnCl_2$ /with regard to FOL/ 83% of "dry" strength /45.4 Mpa/ are attained in 3 days at 24°C, while the hardener used so far /urea nitrate/ results in attaining a strength of merely 37.4 MPa with a moisture content below 2% /with regard to FOL/.

In the case of lower water contents /up to 12.5% with regard to FOL/ BC can be diluted in FOL before being added to the mixture, in the case of major water contents it is
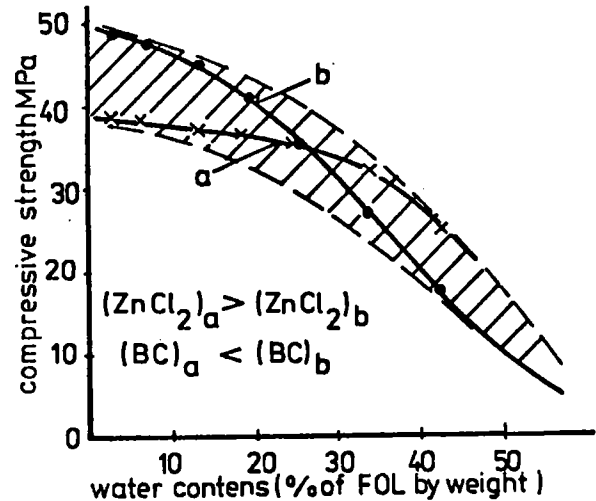

Fig. 1 The relation between compressive strength of PC and water contents in FOL

more suitable to dilute BC in the FAL. Should it be necessary to prolong the workability period /pot life/, BC is addded to the fal even in the case of lower moistur content.

Optimum mixture composition for attaining maximum conversion at a normal temperature /25°C/ in a sufficient lylong period elapsed from the beginning of hardening /t ensure the necessary workability /for the two above mentioned moisture contents values is given in Table 4.

Table 4

Water/FOL /% by weight/	25	12.5
FOL	10	10
FAL	1.5	1.5
BC	1.5	1.5
$ZnCl_2$	1.2	0.7 – 1.0

According to the binder:filler ratio the strength attainable varies. Compressive strength, for example, varies from approximately 45 MPa for the 1 : 9 /by weight mixture to approximately 70 MPa for the 1 : 6 /by weight/ mixture for 1.5% and 2% moisture content respective /with regard to the filler/, etc. After one-hour compressive trength attains approximately 1/3, after 24 hours 2/3 of the 3-day strength.

Using the described system it is possible to apply furan resin concrete even in extreme situations, in which optimum polymerization conditions /i.e. dry components and environment and a temperature of over 15°C/ cannot be ensured, e.g. in speedy repairs of highway or airport sur faces, sewers, reservoirs, etc. In such extreme condition furan resin concrete, with its mechanical properties and homogeneity, exceeds the resin concretes with binders of other resins.

BIBLIOGRAPHY

/1/ Dunlop,A.P.,Peters,F.N.,The Furans, New York, 1963
/2/ Berthelot et Rivals, C.R., 120, 1086/1895/
/3/ Marcusson, J., Z.angew.Chem., 52, 113 /1919/
/4/ Marcusson, J., Z. angew.Chem.,54, 542 /1921/
/5/ Marcusson, J., Z.angew.Chem., 58, 869 /1925/
/6/ Červinka, O., Dědek,V., Ferles, M., Organic Chemistr /in Czech/, SNTL, Prague, 1969, p. 531
/7/ Volmert, B., Principles of Macromolecular Chemistry /in Czech/, Academia, Prague, 1970, p.448
/8/ Bareš, R.A., Navrátil, J., Les bétons de furane et leurs applications, Cah. du Centre Scient.et Techn. du Batiment, 647, No. 76, 1965
/9/ Hess, P.H., 54th Annual Fall Technical Conference of

the Society of Petroleum Engineers of AIME, Sept.
1979, SPE 8213, 1979

/10/ Sugama, T., Kukacka, L.E., Horn, W., Properties of
water compatible furfuryl alcohol polymer concrete,
BNL-28490

/11/ Bareš, R.A., Vašíček, A., Use of wet aggregates for
furan resin concrete - Berol and other products /in
Czech/, TU Priemstav, 19, 1982