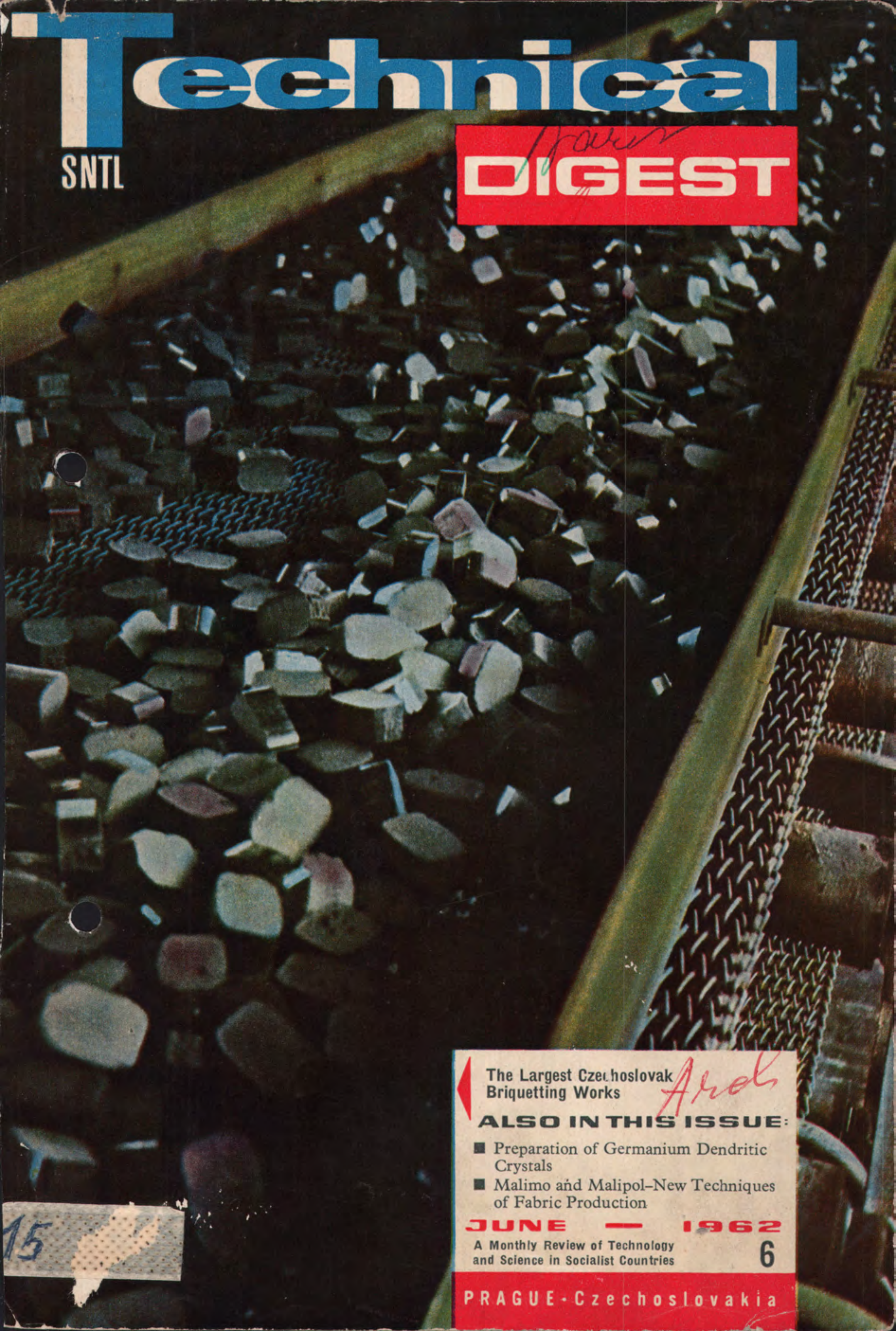
Technical DIGEST

SNTL



The Largest Czechoslovak Briquetting Works

ALSO IN THIS ISSUE:

- Preparation of Germanium Dendritic Crystals
- Malimo and Malipol–New Techniques of Fabric Production

JUNE — 1962

A Monthly Review of Technology and Science in Socialist Countries

6

PRAGUE - Czechoslovakia

ČSA - *LINKING SIX HISTORIC CITIES*

offers: swift comfortable flights
reliable service
traditional hospitality

via Czechoslovak Airlines TU-104 A

Departures from Prague to
South-east Asia each Wendesday
Return to Prague each Friday

BEROL

A FURAN - BASE BUILDING MATERIAL

Richard Bareš *and* **Jiří Hošek**

Institute of Theoretical and Applied Mechanics, Czechoslovak Academy of Sciences, Prague

Plastics are finding an ever increasing field of application in the building industry. To the initial uses (as wall lining, flooring, plumbing material, etc.) are now added the admixture of various disperse substances with intent to modify the properties of traditional building materials and the insulation of structures by plastics resistant to aggressive industrial materials and wastes.

The insulation of load-bearing structures has lately received particular attention. Attempts are being made to obtain structural materials that would not require additional protection against the action of given chemical media and would thus simultaneously bear the load and insulate against chemical effects.

At the Institute of Theoretical and Applied Mechanics, this work resulted in the preparation (in 1959) of BEROL, a new structural and insulating material; it is similar to gravel-sand-cement concrete and is obtained by combining an anorganic component, a mixture of gravel and sand, with an organic one – a furyl alcohol resin (furol resin)①.

Berol is notable for its excellent chemical resistance (to acids, bases, effluents, salt solutions and some solvents) as well as high strength. It may thus be employed in structures exposed to strong aggressive action (in chemical plants, tanks, drain channels, etc.).

FUROL RESIN

The basic material for the manufacture of furol resin is liquid furfuryl alcohol made from furfuryl aldehyde by catalytic hydrogenation in the presence of chromium catalysts. The aldehyde is obtained by hydrolysis of wood waste containing pentosans. The chemical resistance of cured furol resin is superior to that of virtually all other plastics excepting fluoroplasts.

So far, furol resin was mainly used for protective coatings in strongly agressive environments. Thin coating films, however, are very brittle and the danger of cracking due to deformations of the protected structure is considerable. Furol resin is therefore modified with other types of plastics, rubber, asphalt, or organic plasticizers. Even at the cost of somewhat reduced chemical resistance, such modifications are appropriate, because they improve the tensile strength, toughness and elasticity of the protective coating.

BEROL

The manufacture of Berol is similar to that of concrete. Gravel and sand, activated by a catalyst, are gradually mixed with the prescribed quantity of resin (or furyl alcohol), and after complete homogenization this mix is filled into the moulds. Other non-alkalic acid-proof substances may also be used as aggregate. Excessive alkalinity slows down or even inhibits the hardening process, and in some cases the aggregate has therefore to be washed.

Washed sand, gravel, various kinds of slag, clinker, and flue ashes were used in our experiments. Lightweight expanded

---

① Application has been made for a Czechoslovak patent.

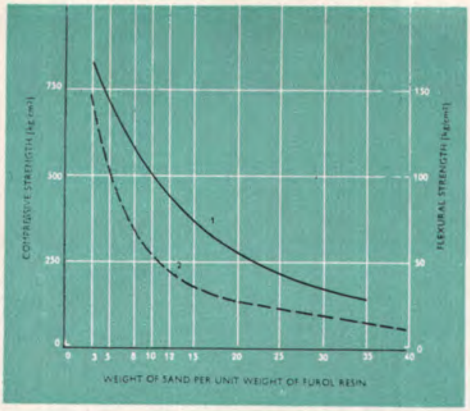


Fig. 1. *Dependance of compressive and flexural strength on resin-to-sand ratio. (Hardening at 50–60°C and 10% R. H.; 7½% of catalyst and 10% of accelerator, referred to the weight of resin)*

1 – compressive strength; 2 – flexural strength

aggregate such as Keramsite and Expandite are particularly suitable.

Even in chemistry proper it is not yet always quite clear how individual factors affect the structure and cross-linking of macromolecules. So much more this is true where resins are only one of several constituents making up a material, as they are in Berol. Most important among the many factors affecting the properties of this material are the type and amount of binder, aggregate, catalyst and accelerator, the processing, the temperature of hardening, the moisture content of environment and aggregate, and the volume-to-surface ratio of the product. Their effects are discussed in the following paragraphs.

1. TYPE OF BINDER

The binder may be introduced into the aggregate in one of two modificationns:

- *as low-viscosity furol resin, that is a partial polycondensate of furyl alcohol, the condensation being completed in the Berol following the addition of the appropriate catalyst;*
- *as furyl alcohol, the entire condensation process taking place in the Berol after the catalyst has been added.*

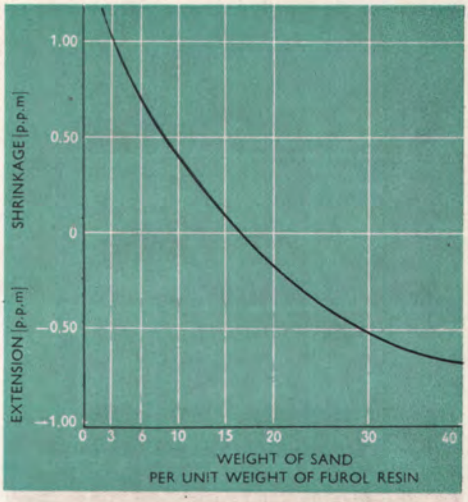
As a rule, the second method is given preference, particularly for reasons of economy; difficulties, however, are also involved, for instance the removal of reaction water, and the outflow of furyl alcohol from the form when the mix is tamped into untight shutterings. Therefore, low-viscosity resins have sometimes to be employed, for instance if a co-polymer with exceptional resistance to some specific chemical action is required.

Either method yields Berol of essentially the same mechanical, physical, and chemical properties. Favourable mechanical properties, especially with respect to the compressive-to-tensile strength ratio, may be obtained by using a mixture of low-viscosity furol resin and furfuryl alcohol.

2. BINDER-TO-AGGEREGATE RATIO

The proportion in which the resin is mixed with the aggregate may vary over a wide range. The dependance of compressive and flexural strength of Berol on the weight ratio of furol resin and sand is shown in *Fig. 1.* Compressive strength was determined for weight ratios of river sand (grain size to 7 mm) to furfuryl alcohol resin, ranging from 3 : 1 to 35 : 1. The moisture content of the sand was about 0.2%. Compressive strength measured after a fortnight was between 830kg[illegible]^2 and 150 kg/cm^2; final hardening proceeded at 50 to 60°C. Compressive strength declines with rising sand content, initially at a fast rate (up to a sand-to-resin ratio of 15 : 1, when the strength is 400 kg/cm^2); subsequently the rate of decline is slower. Most economical are mixes with a sand-to-resin ratio between 15 : 1 and 30 : 1, which give Berol of a compressive and tensile strength that is fully sufficient for normal structures. Further tests, therefore, were only made with a 15 : 1 ratio of the two components.

Fig. 2. *Dependance of relative change in length during hardening on sand-to-resin ratio of mix (7½% of catalyst and 10% of accelerator by weight; hardening at 20°C and 95% R. H.)*



Volume changes during hardening depend on the temperature and humidity of the environment and particularly on the proportion of resin. The dependance of the relative change in length on the sand-to-resin ratio of the mix is shown in *Fig. 2*, while *Fig. 3* illustrates the effect of humidity on longitudinal extension; the added influence of various binder contents is shown in the difference between the individual curves of the family. For the given conditions of curing during hardening, there is no change in length at a sand-to-resin ratio of approximately 17 : 1, while larger resin content causes shrinkage during hardening, lower content swelling. Swelling in leaner mixes is due to the combined effect of shrinkage during hardening and expansion caused by humidity.

The coefficient of thermal expansion of Berol (hardened at 60°C) is given in *Fig. 4* for various sand-to-resin ratios and for a temperature range from 10 to 50°C. [illegible] changes similarly as does compressive or flexural strength; for sand-resin ratios smaller than 10 : 1 the coefficient of thermal expansion rises rapidly and reaches unfavourable values while for mixes with a sand-resin ratio in excess of 10 : 1 its rate of change is considerably smaller. For a 15 : 1 mix the coefficient of thermal expansion exceeds that of concrete by about 50%.

Strain-stress diagrams are given in *Fig. 5* for short-term load tests up to breaking. The shape of these diagrams is less favourable than for concrete, mainly

Fig. 3. *Effect of humidity on longitudinal extension of Berol*

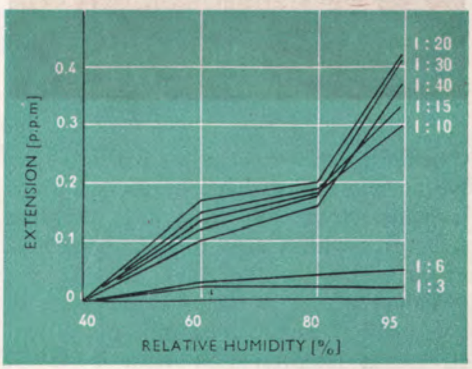
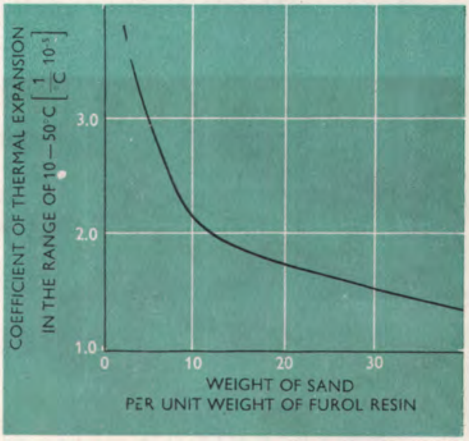


Fig. 4. *Coefficient of thermal expansion of Berol in the temperature range of 10°C–50°C as a function of the resin-sand ratio*



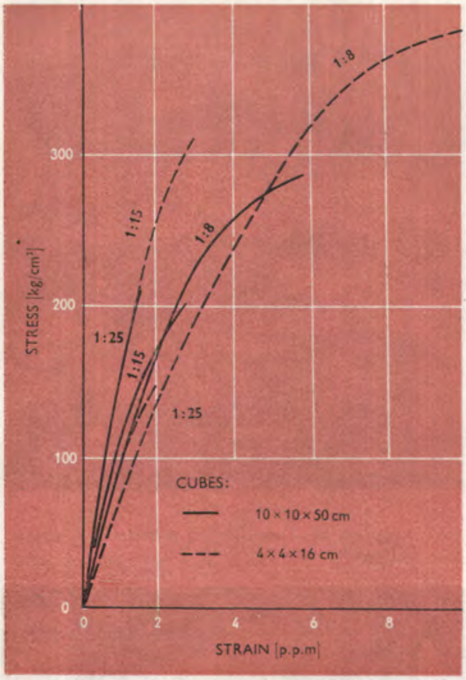


Fig. 5. *Stress-strain diagrams for Berol under short-term load*

considering the extent of the plastic range. Nevertheless, the shape of the diagrams is satisfactory for designing building structures with a view to their behaviour under load.

Values of the modulus of elasticity in compression for various mix ratios and stresses as determined on prisms $4 \times 4 \times 16$ centimetres and $10 \times 10 \times 50$ cm are given in *Fig. 6.* Up to a certain point—shows the diagram—the modulus of elasticity increases with diminishing binder content; the effect exerted by the properties of the aggregate is far more pronounced than in the case of concrete. For a 15 : 1 mix Young's modulus ranges between 100,000 and 200,000 kg/cm² depending on the load.

Creep is an important problem in the application of Berol as a structural material. Long-term tests are still under way, and no final conclusions can be drawn as yet. It appears that creep will diminish with binder content and will largely depend on perfect hardening, that is—indirectly—also on the type of catalyst.

Berol specimens were also subjected to long-term action of various chemical agents (*Fig. 7*). After one year's submersion in aggressive media specimens did not show any visible changes, and their strength was somewhat higher than of test pieces placed in water. *Fig. 8* shows the dependance of compressive strength on the sand-resin ratio, as determined on cubes after three month's submersion in water, petrol and 10% hydrochloric acid. The strength of specimens held in hydrochloric acid was no worse, and that of specimens kept in petrol even better than in water, particularly in the case of leaner mixes. Thus, for instance, compressive strength of a 30 : 1 mix was as high as 200 kg/cm², that is nearly 100% better than after submersion in water. It is obvious from the comparison with results obtained (after 28 days) on specimens not exposed to the action of aggressive media that only saturation with water reduces the strength; for a 15 : 1 mix this reduction is about 40%.

3. TYPE AND AMOUNT OF CATALYST

Various organic and inorganic acids may serve as catalysts. Their choice affects the condensation process and—to a certain extent—the resulting mechanical and physical properties. Optimum results were

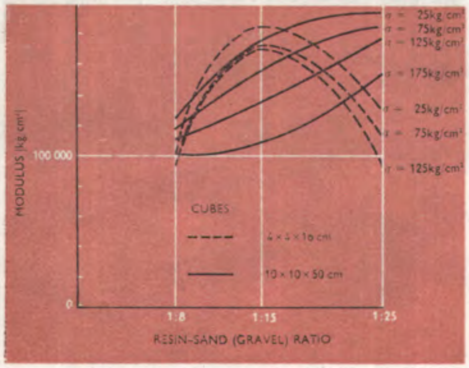


Fig. 6. *Young's modulus of Berol in dependance on resin-sand ratio*

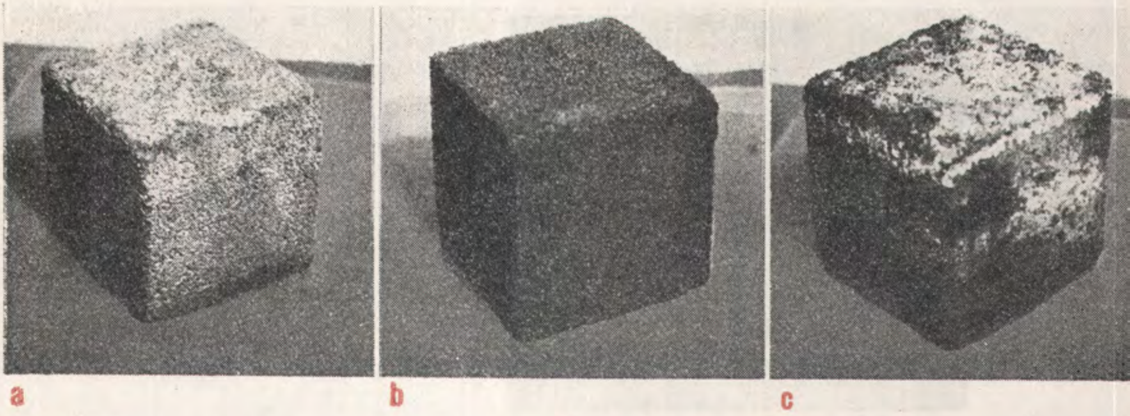


Fig. 7. *Effect of various media on Berol specimens* (a) *2% hydrogen chloride;* (b) *20% hydrogen chloride;* (c) *20% – sodium hydroxide.*

achieved with sulphuric acid, urea nitrate and sulphonic acids such as benzenesulphonic, paratoluene-sulphonic, and betanaphthalenesulphonic acids. It is in particular the time of complete hardening of Berol at normal temperature that depends on the amount of acid of a certain concentration. At a higher temperature a very small quantity of the catalyst is sufficient for complete hardening.

4. TYPE AND AMOUNT OF ACCELERATOR

The inception and completion of hardening may be regulated by accelerators. Fural (furfuryl aldehyde), which is also subject [illegible] condensation and inclusion into the molecular structure, has given the best results. Notwithstanding the ratio at which the accelerator was added, final strength was already reached, as a rule, after seven days; any later increase in strength is insignificant. With dry hardening, especially at elevated temperature, final strength was reached earlier—after some days or even hours.

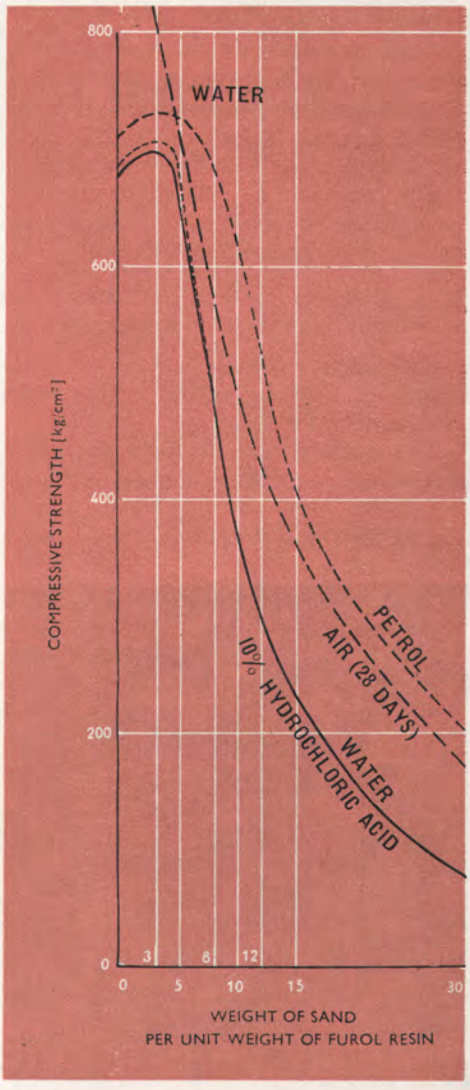


Fig. 8. *Compressive strength in dependance on resin-sand ratio (measured after three months' submersion in water, 10% hydrochloric acid, and petrol as well as 28 days' exposure to air)*

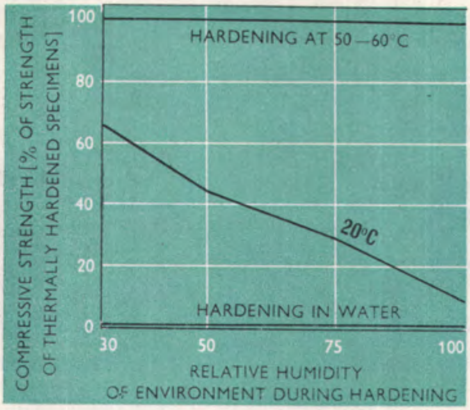


Fig. 9. *Effect of atmospheric humidity during the hardening of Berol on compressive strength. (1 : 15 mix, catalyst 7½%, accelerator 10%)*

5. HARDENING TEMPERATURE

Although the rate of hardening is affected by the temperature, the resulting differences in final properties are not large, provided certain conditions—mainly relating to the relative humidity of the medium and the moisture content of the aggregate—are fulfilled. The optimum temperature for thermal hardening is 50–60°C.

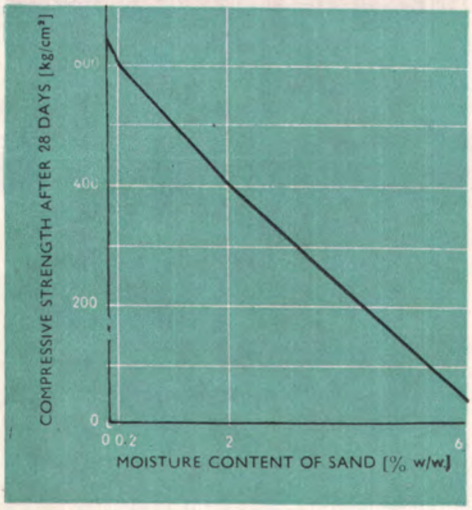
6. HUMIDITY OF ENVIRONMENT AND MOISTURE CONTENT OF AGGREGATE

Both factors greatly affect the final properties of Berol as well as the time taken for hardening.

The condensation of furyl alcohol is particularly sensitive to changes in humidity, and so are therefore the mechanical properties of Berol and its resistance t[illegible] chemical agents (*Fig. 9*). If the compressive strength achieved in dry environment at 50—60°C is considered 100%, the value reached by a specimen submerged in water is virtually zero. An increase of about 20% in the relative humidity of the environment during hardening results in strength reduced by 20%.

The effect of the moisture content of the aggregate (sand in the given case) on the strength of Berol is shown in *Fig. 10*. In dry environment and with absolutely dry sand, compressive strength is about 650 kg/cm² in Berol with a mix ratio of

Fig. 10. *Strength of Berol in dependence on moisture content of aggregate*



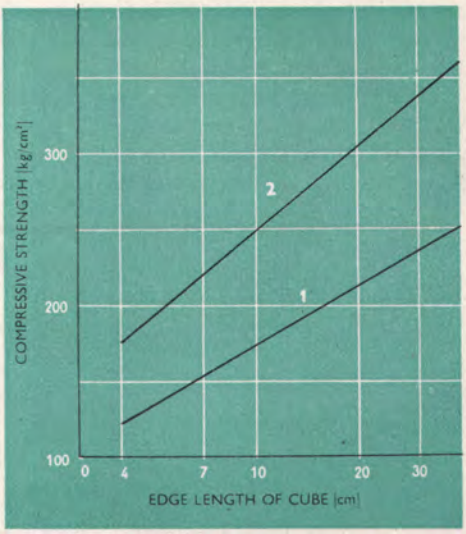
HARDENING AT 20°C 90% R. H.

MOISTURE CONTENT OF SAND [% w/w]	COMPRESSIVE ST[illegible]GTH AFTER 28 DAYS [kg/cm²]
0	88
0.2	80
2.0	1
6.0	0

MIX	1:15
CATALYST	7.5%
ACCELERATOR	10%

■ ■ ■ ■ ■ ■ ■

Fig. 11. *Compressive strength after 7* (1) *and 28* (2) *days in dependence on size of test cubes (1 : 15 mix; doses of catalyst and accelerator 12.5 and 20% respectively by weight; hardening at 20°C and relative humidity of 60%)*



[illegible]: 1. A moisture content of 2% or 6% in the sand reduces the strength to 400 or to 50 kg/cm² respectively.

When hardening at normal temperature (18°C) and 90—95% relative humidity, the same mix gives a compressive strength of only 88 kg/cm² after 28 days, if dry sand is used; and (with the same content of catalyst and accelerator) the mix does not harden at all if the moisture content of the sand exceeds 2%.

7. METHOD OF WORKING UP

In order to ascertain the effect of tamping on the strength of Berol, the test specimens were alternatively worked up manually and with a hammer-type tamping machine (frequency 60 strokes per minute). By increasing the number of strokes from 75 to 300, compressive strength was raised approximately by 2[illegible] The compressive strength of manually worked up Berol is about the same as that of Berol worked up by 200 machine strokes. The effect of working up on the properties of Berol is thus somewhat smaller than with concrete.

The effect of the human factor shows by a fairly wide scattering of results in manually processed Berol. Deviations from optimum compressive strength were up to 28 and 15% with hardening at normal and elevated temperature respectively, while the deviation from the optimum ratio of compressive strength to volume weight was up to 30 and 10% respectively. These data indicate that the hardening speed is primarily affected by perfect mixing, while the final strength is determined by the efficiency of working up.

8. VOLUME-TO-SURFACE RATIO OF PRODUCT

Since the hardening reaction is intensely exothermic, the rate of heat dissipation and thus the volume-surface ratio exercises a considerable influence. The dependence of compressive strength on the size of the test cubes in shown in *Fig. 11.* It is linear if the edge length of the cube is plotted on a logarithmic scale.

9. TYPE OF AGGREGATE

The basic mechanical properties of Berol are greatly affected by the aggregate. Thus, for instance, with crushed basalt and quartz sand in a 15 : 1 mix, up to 1000 kg/cm² compressive strength can be obtained. With ordinary river gravel at the same mix ratio and under optimum conditions maximum strength will be 650 to 700 kg/cm². The strength obtained with light aggregates is tabled below (hardening proceeded at elevated temperature).

Processed aggregates with spherical grain such as Keramsite and Expandite are particularly suitable. With such aggregates even a very small resin content gives Berol of sufficient strength.

Permeability for water, petrol and various acids, and cohesion with steel or glass reinforcement are some of the problems relating to properties as well as practical applications of Berol which are now being studied.

It is the authors' well-considered opinion that building materials with synthetic-resin binders are capable of further development and therefore deserve the research worker's closest attention.

Table

Type of filler	Binder-aggregate [w/w]	Tensile strength [kg/cm²]	Compressive strength [kg/cm²]
Power plant flue ashes	1 : 3	45	9
Power plant slag	1 : 3	158	41
	1 : 5	77	17
	1 : 7	33	8
Incinerator slag	1 : 3	267	54
	1 : 7.5	79	16
	1 : 10	43	5

* * *

THE ANNULAR PISTON SLIDE VALVES *for the Rappbode storage reservoir in the Harz Mountains (GDR) (dia. 1200 mm, weight 20 tons) have been made at the Karl Marx Works in Magdeburg.*