BINDING MATERIALS USED IN MAKING PELLETS AND BRIQUETS

G. R. YOHE

ABSTRACT

This compilation of information about materials that have been used as binders in making pellets, briquets, or other products shaped from powdered or granular substances was prepared for use in the Illinois State Geological Survey laboratories. Although it is not an exhaustive report, other workers also may find it useful.

Information from about 200 abstracts selected from Chemical Abstracts for 1937 through 1963 is included. Both organic and inorganic binding materials are discussed.

The original reference and the Chemical Abstracts citation are given in the list of references. The report is indexed.
In connection with work in progress at the Illinois State Geological Survey, a need arose for a compilation of information about materials that had found application as binders in the making of pellets, briquets, or other articles formed from powdered or granular material.

Although this report is by no means exhaustive, it may be of interest and value to workers in other laboratories. The decision was therefore made to distribute it as an Industrial Minerals Note.

According to Webster's New International Dictionary (2nd edition), a binder is "anything that causes cohesion in loosely assembled substances, as tar, asphalt, or crushed stone in a road."

This definition is somewhat too broad for the present discussion, for it would include such things as water (which serves as a temporary binder for sand as children build their castles at the beach) or mucilage with which we fasten a postage stamp to an envelope. In the broad sense, anything that serves as an adhesive might be called a binder.

This discussion is restricted to substances that can be mixed with powdered or granular solids for the purpose of forming pellets or briquets having reasonably good resistance to weathering and a fair degree of stability in handling. Even with this limitation, it is scarcely possible to assemble complete information, as there are many kinds of materials to be bound, many potential binders, and many purposes for using binders.

Indexes to Chemical Abstracts for 1937 through 1963 were used, but only selected references were examined. For example, under "Binders" only those entries deemed pertinent were looked up, and under headings that refer to materials being bonded, "binders for" references were selected. Numerous topics, including adhesives, cements, fibers, inks, lacquers, lime, mortar, paints, plaster, resins, and rubbers were excluded.

In this review, binders are divided into two categories, inorganic and organic. Under each of these headings, the various binding materials are listed in alphabetical order. This is not completely satisfactory, as many mixtures have been described, some comprising inorganic, some organic, and some both inorganic and organic materials. However, this arrangement is considered preferable to one in which the key words are derived from the materials being bonded, as many binders have been described without reference to the kinds of materials with which they may suitably be used. The index lists binders, materials bonded, and other items such as additives and solvents.

The forces that enable materials to serve as binders are not all of the same nature. Most organic binders function essentially as "glues" or sticky types of adhesive that wet the surfaces of the particles being bonded and thus cement them together. Some such binders are applied as hot liquids and become solid when cool, and others may remain in a more or less viscous liquid state. Some inorganic binders (fusible metals, for example) also function in this manner.
Other binders are solids of very small particle size. Because of their high surface energy these particles adhere firmly to other surfaces, and thus may serve as bonding agents between neighboring particles of the material being bonded. Most binders that function in this manner are inorganic materials; clays, colloidal alumina, and colloidal silica are examples.

Some binding action may involve both of these principles. An ore pellet might possess sufficient "green" or "dry" strength because of surface energy forces, and then be permanently bonded by being heated to a partial fusion stage wherein forces of the first described type come into play.

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INORGANIC BINDERS

ALUMINA

A U. S. patent issued in 1961 to John Bugosh and assigned to the du Pont Company\(^1\) describes the preparation and use of fibrous boehmite, a hydrated alumina (A1OOH). This material, which can carry a positive charge, is used to coat surfaces (e.g., glass, paper) that have been given a negative charge. The coating can then serve to anchor a top coat of other desired material by virtue of its OH groups, its electrical charge, or its fibrous physical nature.

Another publication issued by the du Pont Company\(^2\) describes the binding action of this same material (but calls it "Baymal Colloidal Alumina") and indicates that the boehmite fibrils are approximately 50 angstrom units in diameter and several hundred angstroms long. If an aqueous suspension of these fibrils is applied to a material such as asbestos that is made up of larger fibers or to one composed of spherical or granular particles, the evaporation of water leaves a gel first and then a mat or "felt" of the boehmite fibrils. At points of contact of the fibers or particles, this mat bonds the material together.

ALUMINATES

A Hungarian patent\(^3\) describes the use of alkali aluminates, or aluminates of Zn, Sn, Sb, and Cr which do not contain much free alkali, mixed in a ratio of 1.7:6.0 with neutral or almost neutral solutions of alkali silicates or alkali fluosilicates. After the product is pressed or centrifuged and dried below 100° C, it is subjected to a hydrolytic treatment with water prior to use.

ALUMINUM

Aluminum nitride (AlN), which is useful as a refractory material for contact with liquid or gaseous aluminum, has such a high sintering temperature that common binders are not suitable for bonding it.

A French patent\(^4\) describes the use of powdered metallic aluminum, which is added to the AlN powder with gum arabic, sodium silicate, or ceresin prior to shaping and compressing the pieces. A mixture containing 20, 15, 7, and 58 percent of 25 to 50, 50 to 100, 100 to 200, and -200 mesh aluminum, respectively, is recommended.
ALUMINUM PHOSPHATE AND PHOSPHORIC ACID

Making castable refractories by bonding alumina, zirconia, mullite, beryllium oxide, or silicon carbide with phosphoric acid or aluminum phosphate has been described. A complex amine was used as an inhibitor, and the addition of ammonium fluoride accelerated the setting of the refractory.

ANHYDRITE (See Calcium Sulfate.)

ATTAPULGITE

Zoelitic molecular sieves, described in a German patent, were made by mixing zeolites with 1 to 40 percent of attapulgite (a hydrous magnesium aluminum silicate characterized by a distinctive rodlike particle shape) and water, drying the mixture for two hours at 90° C, and firing the shaped articles at 650° C.

BORATE GLASSES

In the manufacture of abrasive discs, borate glass has been used as a bonding material. The mechanical properties of the abrasives depend upon the percentage of a colorless, needlelike mineral at the contact of the corundum grains with the bond. The amount of this mineral varied with the amount of B\textsubscript{2}O\textsubscript{3} in the bond, and its composition was 3Al\textsubscript{2}O\textsubscript{3}.B\textsubscript{2}O\textsubscript{3}.

A French patent describes the use of alkali metal borosilicates that soften below 1100° C, together with a plastic clay to improve molding qualities, for forming articles from oxides of Al, Zr, and Ti, from diamond, and from carbides of Si, B, W, and Ta. After being molded, the objects are heated to about 1100° C.

CALCIUM CHROMITES

Calcium chromites, prepared by heating mixtures of CaO and Cr\textsubscript{2}O\textsubscript{3} in the presence of air, have been shown to possess hydraulic binding properties.

CALCIUM FLUORIDE

Fluorspar (CaF\textsubscript{2}) has been used as a binder in making abrasive articles and high-temperature bricks.

CALCIUM GERMANATE

Heating a mixture of 2CaO and GeO\textsubscript{2} for three hours at 1250° C forms Ca\textsubscript{2}GeO\textsubscript{4} (calcium orthogermanate), which has "a significant degree of mechanical strength, and may be used as a binder."
CALCIUM OXIDE

Abrasives containing SiO₂ and Al₂O₃ with the addition of trass (a light-colored volcanic tuff occurring especially along the lower Rhine) have been formed with calcium oxide as the binding agent.¹²

CALCIUM AND SODIUM ALUMINATES

A U. S. patent¹³ describes the use of mixtures of calcium aluminate and sodium aluminate for bonding firebrick and refractory aggregates of fused silica, alumina, and kaolin. Such mixtures also bond insulating materials containing asbestos, diatomaceous earth, vermiculite, insulating firebrick, and graphite. The amounts of the mixture of calcium aluminate and sodium aluminate used vary from 10 to 60 percent, and the unfired strength of the objects is better than when calcium aluminate alone is used.

CALCIUM SULFATE

A study of the reactions of anhydrite (calcium sulfate) when used as a binder for building materials has been published.¹⁴

CEMENT P*.JS CLAY

A French patent¹⁵ describes the admixture of clay with such binders as cement in making shaped articles for which mechanical resistance is relatively unimportant. The clay, which should have a grain size below that of the binder and should contain at least 15 percent Al₂O₃ and 40 percent SiO₂, may compose up to 50 percent of the weight of the mixture.

CHROMIUM COMPOUNDS

A U. S. patent¹⁶ refers to the use of chromium ore or chromium compounds as binders for dead-burned magnesite, but is concerned primarily with the use of alkali metal tartarates for improving the quality and strength of such materials. (See Tartrates under Organic Binders.)

CLAY

The effect of clay binders on the oxidation of sintered silicon carbide objects has been compared with the effect of silica gel. The clay binder failed to prevent oxidation below 1230° C.¹⁷

Clay minerals or gels of Al(OH)₃ have been used to make abrasion-resistant microspherical molecular sieve catalysts from synthetic zeolites.¹⁸

A German patent¹⁹ describes the pelletizing of fine ores with a binding mixture consisting of clay and chalk with aqueous ferrous sulfate, starch, and aqueous sodium hydroxide.
FULLER'S EARTH

Fuller's earth ("florigel") kneaded with water to form a sticky, plastic mass has been used as a binder for catalysts and absorbents used in the petroleum industry.26

GLASS PLUS METAL

The binding of diamond abrasives by a mixture composed of a special glass (softening point 2000° to 2350° F) and a metallic portion containing tungsten carbide, iron carbonyl, copper, and small amounts of manganese and graphite is described in a U. S. patent.21

IRON HUMATE

According to a Japanese patent,22 a binder for fuel briquets is prepared by extracting humic acids from peat or coalite with aqueous sodium carbonate and treating the extract with ferrous acetate to get a mixture containing iron humate.

IRON OXIDE PLUS CALCIUM OXIDE

The use of 4:1 to 2:1 mixtures of FeO and CaO in the manufacture of high-silica refractories ("Dinas")23 from crystalline quartzites produces bricks of better and more uniform quality and higher compressive strength than those made with lower proportions of iron oxide in the binder.

LIME

The production of fine-grained lime from coarse limestone by a process of simultaneous heating and tumbling has been described in a German patent.24

The use of a mixture of calcium oxide and gypsum as a binder has been demonstrated.25

MAGNESIUM CHLORIDE

In the use of dolomite for hearth lining in a 5-ton basic electric furnace, magnesium chloride was found to be a better binder than either sodium silicate or tar.26

MAGNESIUM OXIDE

The preparation of magnesium oxide by precipitating with lime water and subsequent calcining at 300° to 400° C is described in a Russian patent.27

Magnesium oxide prepared by firing magnesite has about twice the strength of that from firing dolomite, and the strength is greater when the
Magnesite is fired at lower temperatures (650° to 700° C) than at higher and when fired short rather than long times.  

A U. S. patent describes the manufacture of a refractory bond-forming material for nonacid refractory aggregates by firing a mixture of finely divided MgO and SiO₂ (20 to 60 percent of the latter) for half an hour at 1100° C.

**MAGNESIUM SULFATE**

The change in form that occurs when a dehydrated inorganic salt is converted to the hydrated crystal form is the basis for the recommendation that a partially dehydrated magnesium sulfate be used industrially as a binding material. Setting begins in 3 minutes and is complete in 6 minutes.

**METALS**

A U. S. patent describes the forming of objects from powdered graphite that had been mixed with a diffusionable binder, such as Zr, Nb, Mo, Ti, Cr, Si, or compounds of these which decompose to form the metals. For example, graphite containing 4 percent ZrH₄ was pressed in a die at 4000 lb/sq in, while being heated to 1600° C in a reducing atmosphere and gave a strong, compact object of low porosity.

Titanium carbide articles have been formed with fusible metals as binders. Chromium and silicon adhered to TiC after cooling below the melting point, but nickel and cobalt surrounded the TiC particles more thoroughly. Other metals tried were Al, Be, Nb, Au, Fe, Pb, Mg, Mn, Pt, Ti, and W.

The use of low-melting metals or alloys to bond powdered magnetic metals, such as alnico, has been patented in the United States. The mixture of powder, fusible metal (melting point below 450° C), and ZnCl₂ as a flux is heated to coat the alnico grains, then pressed into a mold at a temperature above the melting point of the binder, and cooled.

**METAL CARBIDES**

A U. S. patent describes the carbide-bonding of graphite articles. A thermosetting synthetic resin is first used to bind the graphite particles into the desired shape. After the resin is cured, the object is heated in a neutral or reducing atmosphere in the presence of carbide-forming elements (Hf, Zr, Ti, V, Ta, Cr, Mo, W, Th, U, B, or Si, or a mixture thereof) to enable the elements to penetrate the object and react to form carbides in situ.

**METAL CARBONYLS**

This process, the subject of a Russian patent, involves bonding metal carbide or nitride powders by treating them with solutions of the carbonyls of the same metals, so that decomposition, presumably at an elevated temperature, results in deposition of the metal that serves as the actual binder.
METAL PLUS GLASS

A French patent describes the agglomeration of diamond powder with a mixture of 80 percent fine metal powder (85 percent Cu, 10 percent Sn, 5 percent Ag) and 20 percent fine glass (72 percent SiO₂, 11 percent Na₂O, 5 percent Al₂O₃, and 12 percent B₂O₃). The mixture is fritted in a reducing atmosphere at 700° to 760° C under pressure of 1 to 4 tons/sq cm.

PHOSPHORONITRILE DICHLORIDE POLYMERS

According to a German patent, polymeric phosphoroniitrile dichloride (PNCl₂)n is used as a binder for abrasives forming abrasive wheels. It is prepared by refluxing 5.3 g NH₄Cl and 20.8 g PCl₅ in 100 cc C₂H₄Cl₂, filtering when evolution of HCl has ceased, recrystallizing the product from C₂H₄Cl₂, and heating it to 36°C. A water-soluble resin was made by heating 11 g hydroquinone, 11 g resorcinol, and 18.6 g H₃BO₃ to 280° C. Thirty-eight grams of this powdered resin, 2 g of hexamethylenetetramine, and 8 g of (PNCl₂)n were mixed with carborundum and formed into a wheel at 175° C.

PHOSPHORUS ACIDS PLUS METAL OXIDES

Equal parts of H₃PO₄ and H₂P₂O₇ were mixed with a dry metallic oxide (MgO and Fe₃O₄ are not suitable, but most others are) in a ratio of 1:3 to 3:1 and heated 5 to 60 minutes at 250° to 400° F; then 2 to 5 percent of a dusting powder such as MgO or MgCO₃ was added and the mixture ground to the desired size. This material, described in a U. S. patent, can be used as a binder or as a molding composition.

PICKLING LIQUORS

Neutralization of sulfuric acid waste pickling liquors and subsequent production of FeSO₄ leaves a residue containing CaSO₄. A possible use for this residue is as a binder.

PORTLAND CEMENT

A Russian patent describes the use of portland cement or alumina cement, with or without the addition of sodium silicate, as a binder for abrasive wheels of quartz, carborundum, and like materials.

POTASSIUM SILICATE PLUS Zn OR Ca COMPOUNDS

A U. S. patent on the bonding of abrasives indicates that a stable, heat-resistant binder that is self-setting at room temperature and resistant to discoloration in moist climates consists of a mixture of about 350 parts of a high-ratio potassium silicate (SiO₂/K₂O less than 2), about 100 parts of ZnO, ZnCO₃, or CaCO₃, and 1.5 to 2 parts of a wetting agent such as sulfonated castor oil.
SALT HYDRATES

According to a German patent,\textsuperscript{42} ores may be pelleted by mixing them with a binder that consists of a supersaturated solution or melt of a hydrated salt, of which the liquidus temperature is above room temperature.

SILICA

The preparation of colloidal silica sols in which the silica is of very small particle size has been described in a U. S. patent.\textsuperscript{43} The use of such sols, with gelation promoted by an acid or a "latent acid" (such as formamide, which yields formic acid and ammonia on hydrolysis), has been recommended for the binding of ore pellets,\textsuperscript{44} and may be of particular interest in pelletizing calcium fluoride for use in the steel industry.

SILICATES (See also Sodium Silicate.)

Granular lead oxides are prepared, according to a German patent,\textsuperscript{45} by mixing PbO or Pb\textsubscript{2}O\textsubscript{4} with 5 to 15 percent of a wetting, binding, and hardening agent and heating the mixture to 300° C with a vibratory motion. Sodium or potassium silicates are among the suitable agents listed.

SILICIDES

Carbon articles such as electrodes can be bonded together by application of a collodion-acetone suspension of Si and/or one or more of such silicides as those of Mo, W, Ti, Zr, Ta, and Cr and heating to 1900° to 2100° C in an argon atmosphere.\textsuperscript{46}

SILICON CARBIDE

Carbon articles were made by mixing amorphous carbon with SiC or an inorganic carbide, molding, and heating to above the temperature of decomposition of the carbide.\textsuperscript{47}

SODIUM SILICATE (See also Silicates.)

A German patent\textsuperscript{48} describes a process of preparing granular superphosphates from powder by adding 1 percent of water-free sodium silicate and 5 percent 7-hexachlorocyclohexane in the presence of 2 to 3 percent water and mixing well in a granulating apparatus. The drying and setting process is fairly rapid. The use of sodium metasilicate or other alkali silicates is also described in a Spanish patent.\textsuperscript{49}

Sodium silicate has also been used with a variety of other materials as additives. For example, a Japanese patent\textsuperscript{50} calls for the use of a mixture of 30 kg of commercial Na\textsubscript{2}SiO\textsubscript{3}, 1 kg of carnauba wax, 10 kg of water, 15 kg of kieselguhr, 22 kg of CaCl\textsubscript{2}, 17 kg of K\textsubscript{2}SO\textsubscript{4}, and 20 kg of talc powder. The mixture is ground to -100 mesh. Use of 30 kg of this mixture with 200 kg of sand and a suitable amount of water gives a molded product that does not freeze in winter and is waterproof and fireproof.
A U. S. patent \(^{51}\) referring to the agglomeration of iron ores in the blast furnace describes the use of sodium silicate alone or mixed with molasses or glucose as a cementing agent to decrease the formation of flue dust in the blast furnace, and states that as little as 0.1 percent of 40° Be water glass makes a measurable difference in flue dust formation.

For making fuel briquets, a German patent \(^{52}\) describes the use of sodium silicate containing citric acid.

A U. S. patent describes the binding of organic and inorganic materials, including refractories. \(^{53}\) This is done by dissolving tartaric, citric, or lactic acid in water to give a pH of about 2.5 and adding 1000 cc of this solution to 20 to 30 cc of a solution of a polyhydric alcohol and 30 cc of a glucose sirup. This mixture is then added to 33.5° to 67.5° Be sodium silicate until a pH of 10 to 12 is obtained. Other binder compositions of a similar nature also are described. The aggregate and binder are mixed, compressed, solidified at about 150° C, and fired at 1000° to 1850° C. The articles possess good storage characteristics and are insensitive to frost.

**WOLLASTONITE**

This native calcium metasilicate \((\text{CaSiO}_3)\) was used in making abrasive wheels. \(^{54}\) The materials were heated to various temperatures, quenched, pulverized as needed, shaped under pressure, and sintered at 800° C. Decreasing the particle size and increasing the shaping pressure gave stronger articles, but the compressive strength was decreased if the temperatures used prior to quenching were increased from 1200° to 1800° C.

**ZINC SULFATE HYDRATE**

Rapid setting and intense hardness were observed for binders consisting of anhydrous \(\text{ZnSO}_4\) and water, but strength was lost completely under conditions that permitted the subsequent loss of water and reversion to the anhydrous salt. \(^{55}\)
ORGANIC BINDERS

ALGINIC ACID

A German patent on the manufacture of fuel briquets indicates that the molding properties of bituminous coals or petroleum or pitch semicoke can be improved by the addition of alginic acid or its salts or gels. It can be applied in the form of an emulsion with organic agglutinants such as tar, pitch, or anthracene oil, and the addition of milled soft pitch is recommended with lower volatile fuels.

ALKALI CELLULOSE

A German patent describes the preparation of weather-resistant briquets by treating coal, coke, or wood charcoal with a 2 percent solution of sulfided alkali cellulose, heating at 50° C, adding some water if necessary, and then pressing.

AMINES

According to a U. S. patent, solid particles such as coal, fly ash, or ceramic materials that contain "digestible matter" may be bonded by mixing them with amines such as \( \text{RNH}_2 \), where \( R \) is aliphatic and contains not more than 12 carbon atoms, or \( \text{H}_2\text{N(CH}_2\text{)}_n\text{NH}_2 \), where \( n \) is not more than 6.

ANTHRACENE-SULFUR

When anthracene oil was heated for 5 to 7 minutes at 280° to 290° C with 3 percent of sulfur, a binder suitable for use in making coal briquets was obtained. When 0.1 to 3 percent of this binder was added to the coal charge, briquets having improved strength and water resistance were obtained.

ARALDITE

The physical and chemical properties of Araldites (epoxy resins) as binders have been discussed in two reports.

ASPHALT

Because of a scarcity of tar in France, experiments on the use of asphalt as a binder for briquetting fine coal dust have been carried out.

A French patent describes in detail the preparation from a Kuwait crude oil of an asphaltic bitumen that is suitable for use as a binder for coal fines.
The modification of petroleum asphalts by air oxidation at 235° to 280° C to increase their viscosity and adhesiveness has been described in two Russian articles;64,65 such products are used in making coal briquets.

Asphalts with various additives have been used as binders. For example, a British patent66 calls for powdered casein and magnesium silicate to be stirred into melted asphaltic material. Salt and sugar may also be added. The resultant binder is suitable for use with rock aggregates for pavements.

A liquid binder, capable of coating damp or unheated aggregates, was made by blending 10 to 50 percent of a viscous, nonvolatile hydrocarbon oil with 20 to 60 percent of a volatile petroleum distillate and mixing the blend with 15 to 40 percent of a powdered, hard asphalt; this is the subject of U. S. patents.67

Another U. S. patent68 deals with the admixture of phenolic compounds and a metal oxide such as PbO with asphalt in the manufacture of binders useful in road construction.

Oleylamine in amounts of approximately 2.5 percent added to asphalt improves binding action, especially for acidic or moist aggregates.69

The use of 0.1 to 5 percent of a substituted tetrahydropyrimidine (i.e., 2-heptadecyl-4,6,6-trimethyl-3,4,5,6-tetrahydropyrimidine) to improve the binding characteristics of asphalt also has been patented in the United States.70

Still another U. S. patent72 involves the addition of a solvent to asphalt. The solvent is of the paraffinic hydrocarbon type, b.p. 50° to 200° C, and the solvent action is increased by admixture of small amounts of oxygenated solvents of the ether, ester, or ketone type.

**BITUMENS**

Numerous articles have been published on the use of various bituminous materials as binders. Some of these deal with general features of binding action, while others cite specific mixtures and applications. In one of the former type,72 water resistance is discussed in terms of adhesion between the mineral aggregate and the binder. Adhesion is defined as the resultant of the interfacial tensions of water and the binder relative to the aggregate. Negative values indicate that water tends to displace the binder, as it does when the aggregate is hydrophilic. With positive values, the aggregate is hydrophobic and the binder is not displaced readily by water. Chemical interaction between binder and aggregate is an important factor; the hydrophobic character accompanying good adhesion is enhanced by reaction between basic oxides of the aggregate and acidic groups of the binder to give water-insoluble compounds.

In using bitumens instead of pitches as binders for fuel briquets, it is important to develop procedures that work best for the particular bitumen used.73 A Nagylenglyl crude oil bitumen,74 although inferior to coal tar pitch for binding coal briquets, could be used satisfactorily, especially when applied in the molten state by spraying.
According to a German patent,\textsuperscript{75} ores, coal, lime, or mixtures thereof are briquetted with a distilled bitumen having a penetration (depth of penetration of a needle of specified shape under controlled conditions of load, temperature, and time. See ASTM Designation D5-52) of 20 to 30 at 25° C. The powdered material is wet, mixed with the hot liquid bitumen, and homogenized before pressing.

Several shale bitumens were studied as possible binders for coal briquets;\textsuperscript{76} those of lower density (about 1.1) and softening temperature (46° to 50° C) were not satisfactory, but one with a density of 1.17 and softening temperature of 87° C produced briquets of high heat- and water-resistance that were superior in mechanical strength to those made with coal tar pitch. Another study of shale bitumens\textsuperscript{77} showed that those of high softening temperatures could be used directly, while those of lower softening temperatures could advantageously be applied as pastes with lime.

Bitumen emulsions also have been much used as binders. Coal fines, for example, have been briquetted satisfactorily after being sprayed with an emulsion of petroleum bitumen, water, and an emulsifier;\textsuperscript{78} pressing was at 250 kg/sq cm while the material was hot, and the effects of varying the particle size, moisture content, amount of binder, and other factors were studied.

A U. S. patent\textsuperscript{79} deals with the use of a quick-breaking oil-in-water type of emulsion of bitumen for binding mineral aggregates. The bitumen is emulsified in combination with NaOH and an alkali metal phosphate. A similar type of emulsion used for bonding hydrophilic aggregates and incorporating 0.05 to 0.5 percent of sodium dichromate is said to form a particularly strong bond with the aggregate.\textsuperscript{80}

Another U. S. patent\textsuperscript{81} involves adding Na$_3$PO$_4$ to a low-viscosity, quick-breaking, clay-free bituminous emulsion to slow down the breaking to allow sufficient time for mixing with the aggregate, fibrous filler, and other materials, while a French patent\textsuperscript{82} describes the use of such emulsions with the addition of an emulsion-breaking agent to give controlled breaking at the desired time. A general theoretical discussion of the adhesion of bitumens to rock aggregates and the use of emulsifying agents has been published.\textsuperscript{83}

Bitumens have been modified by the incorporation of various types of additives. A German patent\textsuperscript{84} claims improved adhesion of bituminous binders to aggregates by the addition of small amounts (0.01 to 1.0 kg/1000 kg of aggregate) of an aqueous dispersion containing, preferably, 10 to 15 percent of a water-insoluble amine or amide. For example, an especially useful dispersion contained 75 percent water, 10 percent long-chain amine, and 15 percent of a 21 percent alkyl sulfate solution.

A French patent\textsuperscript{85} also calls for the admixture of amines to improve the adherence of bitumen binders, citing RNH$_2$, RR'NH, and RR'R''N, where R, R', and R'' are hydrocarbon radicals of at least 13 carbon atoms.

Two French patents\textsuperscript{86,87} claim to improve the adhesiveness of bituminous binders by the addition of 0.2 to 5 percent of salts of primary or secondary amines that do not decompose on heating, or 0.1 to 5 percent of reaction products of polyamines with mineral or organic acids. These salts may be added as such or formed in situ by incorporating the acid and base separately into the bitumen solution.
A German patent\textsuperscript{88} specifies as a binder for making coal or coke briquets a mixture of bituminous hydrocarbons, sulfidic benzene derivatives, sulfidic benzene homologs, and aliphatic halohydrocarbons. The components were mixed and heated in an autoclave while being stirred rapidly.

A blend of petroleum bitumen and a fraction from Ladkin asphaltite was said to be thermally and chemically a more stable binding material than coal tar pitch.\textsuperscript{89}

The addition of calcium phenolates to avoid the undesirable effects of naphthenic acids in bitumens has been cited by a German patent.\textsuperscript{90} Thus 51 kg of CaO was dissolved in 8.5 metric tons of boiling commercial creosote oil with simultaneous removal of 25 kg of water (and a small amount of oil) by distillation. After cooling, the oil was added to 41.5 tons of bitumen "B-80" and stirred at 150° C. Adhesives of the amine type were then added.

A French patent\textsuperscript{91} describes the preparation of bituminous binders having good adhesion toward mineral aggregates and metals. In the process, 0.5 to 2.0 percent of heavy metal soaps of high molecular weight organic acids, such as Fe or Pb oleates or naphthenates, was added to the bitumen. This binder was used as a preliminary coating; a further quantity of binder not containing such soap was then added.

The addition of unslaked lime to bitumen to produce a slow-setting binder is described in a U. S. patent.\textsuperscript{92} Another U. S. patent\textsuperscript{93} covers the use of a heavy bitumen to which an organic nitro compound has been added for making carbon electrodes.

The improvement of adhesiveness of bituminous binding agents by the addition of organic silicon compounds, such as $(\text{CH}_3)_x(\text{CH}_2\text{O})_y\text{Si}$, where $x + y = 4$, is claimed in a German patent.\textsuperscript{94} The silane may be applied to the rock aggregate prior to addition of the binder, or it may be mixed with the bitumen.

\textbf{BUTADIENE-CHLOROPRENE}

The bonding of abrasive articles by the use of polymerized chloroprene mixed with a butadiene monomer and an unsaturated ketone has been claimed in a U. S. patent.\textsuperscript{95}

\textbf{CARBOHYDRATES (See also Cellulose Derivatives and Starch.)}

The preparation of carbohydrate ethers or esters for use as binders has been described in a U. S. patent,\textsuperscript{96} and carubin (locust bean gum), which is about two-thirds mannose and one-third galactose and almost completely water-soluble, has found application as a binder in the ceramic and mining industries.\textsuperscript{97}

\textbf{CASEIN}

A mixture of casein with 30 percent by weight of portland cement has been patented in Russia as a binder for making abrasive wheels.\textsuperscript{98}
CASSAVA FLOUR (See Manioc Flour; Sulfite Liquor, and reference 177.)

CELLULOSE DERIVATIVES

A German patent describes the preparation of a polysaccharide binding agent, suitable for use in textiles, papers, and paints, from inorganic reactants and cellulose derivatives. For example, 25 parts of sodium carboxymethylcellulose, 10 parts of $\text{Al}_2(\text{SO}_4)_3$, and 5 parts of $\text{Ca(OH)}_2$ or 3 parts of MgO form a useful dispersion when added to water and stirred.

COAL PLUS AMINES (See also Amines; reference 58.)

A mixture of coal and amines has been patented in the U. S. as a binder for ceramic materials. It is hardened by heating it to a temperature below the decomposition temperature of the coal used.

COAL HYDROGENATION PRODUCTS

According to a Russian patent the product obtained by hydrogenating a humus coal at 350° to 380° C and 50 to 100 kg/sq cm may be used as a binder for briquetting coal.

DRIYING OILS PLUS ADDITIVES

A British patent mentions a number of drying oils (for example, linseed, soybean) which may be mixed with about 15 percent Isano or Boleko oil, heated to the desired viscosity (5000 cp at 20° C, for example), treated with 0.1 percent Co and 0.3 percent Pb driers, and used in about 2 percent amounts with quartz sand to make foundry cores.

EPOXY RESINS (See also Araldite.)

A German patent claims that resins made by curing epoxy alkyl esters of polybasic aromatic acids with polycyclic aromatic amines can be used as bonding agents for metals and other materials. For example, 100 g of diglycidyl terephthalate melted with 25 g of benzidine was heated at 90° to 100° C and degassed for 5 minutes at 5 to 20 mm, poured into molds, and cured at 140° C for 60 minutes.

Another patent describes a cement for abrasives that is made by the condensation of vinylcyclohexene dioxide with pyromellitic anhydride.

A U. S. patent describes a binding mixture of 5 parts by weight of an epoxy resin prepared by the reaction of 2,2-bis(4-hydroxy-3-allylphenyl)propane and epichlorohydrin, 3 parts of a high molecular weight (3,000 to 10,000) polyamide prepared by the reaction of dilinoleic acid and ethylenediamine, and 1 part of a liquid polysulfide prepared by the reaction of bis(2-chloroethyl)-formal and $\text{Na}_2\text{S}_x$ cured for 10 to 12 seconds at 180° C. This had excellent strength and good resistance to water and ethylene glycol.
FURAN DERIVATIVES

A U. S. patent\textsuperscript{108} claims that molding sands or abrasive granules may be bonded with 4 percent of a mixture such as 75 parts of furfuryl alcohol, 25 parts of maleic anhydride, 5 parts of urea, and 0.5 part of NH$_4$Cl. The resulting mix was cured in an oven at 300° F.

GLYCEROL

A German patent already cited\textsuperscript{45} describes the preparation of granular lead oxides by mixing the oxide (FbO or Pb$_2$O$_4$ or both) with 5 to 15 percent of a wetting, binding, and hardening agent and heating them to 300° C with a vibratory motion. Glycerol, as well as dispersions of high polymers (e.g., polyvinyl chloride in acrylic acid or polystyrene, sulfite liquor or molasses wastes), is listed as a suitable additive. Glycerol also may be used as a binder in refractories and ceramic-bonded abrasive compositions.\textsuperscript{107}

GLYCOL ESTER DERIVATIVES

A binder for uniform, very hard, dense, abrasive forms is made from an unsaturated polymer of a glycol and an unsaturated polybasic acid, copolymerized with a vinyl monomer and styrene in the presence of benzoyl peroxide (U. S. patent).\textsuperscript{108}

GUMS, NATURAL (See Shellac.)

HUMIC ACID AND HUMATES

A Russian patent\textsuperscript{109} describes a binder for coal briquets that is obtained by treating brown coal ground to 0.5 mm particle size with a 0.1 percent solution of NaOH or NH$_4$OH. This is similar to the preparation described 15 years later as "new"—a sodium humate made by fine grinding of coal in an alkali;\textsuperscript{77} the amount of this used in briquetting was kept below 1.5 percent to avoid tackiness on the press.

Other experiments on the use of humates as fuel briquet binders\textsuperscript{110} indicate that the crushing strength of the product depends upon the cation accompanying the humate ion; with Na a maximum of 40 kg/sq cm is attained, but with Al, NH$_4$, Fe, and Ca it is 20 kg/sq cm or less. Optimum amounts of the binder are 3 to 6 percent.

HYDROXYAMINE DERIVATIVES

A British patent\textsuperscript{111} describes binding agents for tar and bitumen that are made by treating (HOC$_2$H$_4$NHCH$_2$H$_4$)$_2$NC$_2$H$_4$OH with stearic or oleic acid at 140° to 160° C.
LIGNOSULFONATES

A study of the variation of properties of lignosulfonates with varying molecular weights showed that with increasing molecular weight their binding strength in iron ore pellets increased.112

LUPINES

A Hungarian patent113 specifies that if seeds of lupines or soybeans are steeped in an acid solution for 8 to 12 hours, separated from the liquid, disintegrated, partly freed (if desired) of their oil content, and added to powdered coal in amounts of 1.5 to 4 percent, suitable binding action is achieved.

MANIOC FLOUR PLUS MOLASSES

A French patent114 describes the binding of charcoal briquets with a mixture of 560 g of manioc flour, 433 g of molasses, 4 g of 30 percent NaOH solution, and 3 g of 30 percent formaldehyde solution.

MOLASSES

A French patent115 dealing with coal briquets describes as the binder used a hardened product obtained by dehydration of molasses or other sugar residues followed by polymerization at an elevated temperature in the presence of a catalyst. The brittle product is then ground to a powder, which may be used alone or mixed with tars, bitumens, resins, or with a fermentation inhibitor.

NITROPHENOLS

Although the nitrophenols are apparently not used alone as binders, a Japanese patent116 claims that the addition of a "phenylnitrophenol compound" to a binder for the manufacture of molded products of carbon and graphite improves their hardness and bending strength.

ORGANOSILICONS

A U. S. patent117 claims polymers of siliconols, alkoxy silicons, siliconacrylates and other organosilicons as binders for abrasives. They may be used with or without nonsilicon resins.

PETROLEUM OXIDATION PRODUCTS

Binders that have kerosene or white spirit oxidation products as their base are prepared by the oxidation of hydroxy acids with xylitol or its anhydride in the presence of H₂SO₄, NaHSO₄, or a sulfonic acid to thicken the product. Drying of the esterification product is hastened by dissolving it in solvent naphtha containing 1 to 2 percent litharge (Russian patent).118
PETROLEUM PITCH

A binder described in a French patent\textsuperscript{119} is composed of a mixture of petroleum pitch and coal tar stabilized with bituminous shale pitch.

A British patent\textsuperscript{120} describes a petroleum pitch suitable for making coal briquets. The pitch is made by air oxidation of a residue from the vacuum distillation of petroleum (or a bitumen obtained by deasphalting such a residue) at $340^\circ$ to $400^\circ$ C and atmospheric pressure. Steam injection is used to control the temperature, sweep out volatile substances, and prevent the deposition of coke.

A U. S. patent\textsuperscript{121} deals with binders for carbon electrodes; these binders (softening point 70$^\circ$ to 120$^\circ$ C, specific gravity 1.2 to 1.3, and H/C ratio less than 1) are prepared by mixing a cracked petroleum fraction, containing at least 50 percent by weight aromatic compounds and having a minimum boiling point of 650$^\circ$ F, with a partially hydrogenated cracked fraction also containing at least 50 percent aromatic compounds and having a minimum boiling point of 700$^\circ$ F. The mixture is then thermally and noncatalytically cracked at 100 to 2500 lb/sq. in. gage and 800$^\circ$ to 1000$^\circ$ F, and the product stripped at less than 525$^\circ$ F and 20 mm pressure to produce the binder.

Binders useful as substitutes for tar in the manufacture of solid fuels are described in a French patent\textsuperscript{122}; they are made by mixing coal dust of 0.5 to 1 mm particle size with petroleum pitch and, optionally, oil tar, $\text{Al}_2(\text{SO}_4)_3$, and an oxidic mineral containing 8 percent carbon, 6 percent $\text{Fe}_2\text{O}_3$, 31 percent $\text{Al}_2\text{O}_3$, 48 percent $\text{SiO}_2$, and 7 percent $\text{H}_2\text{O}$.

PHENOL-ALDEHYDE RESINS

In the preparation of phenol-aldehyde resin binders, various phenolic compounds or crude phenol-containing mixtures and various aldehydes have been used. An example of the application of a crude mixture is seen in a French patent.\textsuperscript{123} To 1000 kg of a crude wood tar containing 3.5 percent acetic acid, ammonia was added in sufficient amount that 10 to 15 kg of acetic acid remained unneutralized. This provided a mixture of acetic acid and its ammonium salt to serve as a catalyst for the condensation reaction. Then 70 kg of acetaldehyde was added slowly, with stirring, under an atmosphere of nitrogen, the temperature was raised slowly to 70$^\circ$ C and maintained at that point, with stirring, for 5 hours. A slow stream of air was then passed through the mass and the temperature raised to about 110$^\circ$ C. After 14 to 16 hours, a product was obtained that softened at about 60$^\circ$ C, melted at 71$^\circ$ C, and was useful as a binder for coal dust.

A binder for charcoal briquets described in a Japanese patent\textsuperscript{124} was made by heating a mixture of 100 parts crude phenol, 100 parts formalin, and 2 parts $\text{H}_2\text{SO}_4$ for 1 hour at 60$^\circ$ C, washing with an equal amount of water, allowing the residue to stand 2 hours with 100 parts of methanol and 5 parts of 38 percent $\text{NH}_4\text{OH}$ and then overnight with 10 percent NaOH in methanol.

A British patent\textsuperscript{125} involves the use of formaldehyde with a coal tar acid fraction containing phenol (phenol:formaldehyde ratio of 1:1.5 to 1:2.2) and condensation in aqueous NaOH. Lignin, starch, cellulosic material or other carbohydrates may be used as extenders, and the coal briquets are cured by heating to 140$^\circ$ to 160$^\circ$ C. The briquets are weather-resistant.
A modified phenol-formaldehyde resin, containing about 10 percent of o-chlorophenol, is claimed as a binder for abrasives in a U. S. patent.\textsuperscript{128}

A British patent\textsuperscript{127} claims that the bonding of such materials as glass fibers by means of a phenol-aldehyde resin can be greatly strengthened by incorporating 0.1 to 0.5 percent of an organosilicon compound of the formula $R_nSiX_4-n$, where $R$ is an alkyl, aryl, or alkylaryl radical containing one or more OH or NH$_2$ groups reactive with the resin, $X$ is alkoxy, aryloxy, OH, or a halogen, and $n$ is 1, 2, or 3.

A Russian patent\textsuperscript{128} relates to the use of a mixture of powdered phenol-formaldehyde resin and rubber for bonding grains in making abrasive articles, and a U. S. patent\textsuperscript{129} describes the bonding of metal oxides or magnetic compositions by the use of a 2:1 mixture of phenol-formaldehyde and urea-formaldehyde resins along with Ca, Zn, or Bu stearate, carbowax plasticizer, and a little water.

**PHENOL BORATES AND PHOSPHATES**

The bonding of abrasive grains in making grinding wheels may be accomplished, according to a U. S. patent,\textsuperscript{130} by means of boric and phosphoric acid esters of various phenols. In one example a resin was made from 12.1 parts of monophenyl phosphate, 11 parts each of resorcinol and hydroquinone, and 14.3 parts of boric acid. The mixture was refluxed to drive off water, and the temperature was gradually increased to 200° C within an hour to yield a brown, somewhat pliable, sticky resin. The resin was mixed with 2 percent hexamethylenetetramine, and carborundum grains added until the resin was 10 percent of the mixture. This was formed into a wheel, cured 1 hour at 175° C and then at 200° C.

**PITCH (See also Petroleum Pitch.)**

Various pitches and pitch combinations have found extensive use as binders, probably because of the ready availability and low cost of the pitch as well as its desirable physical and chemical properties. Although a majority of these applications seem to be in the realm of making fuel briquets, the use of pitch as a binder is by no means restricted to these materials.

According to a British patent,\textsuperscript{131} a binder is produced by oiling back a pitch, removing water and part of the oils by distillation, extracting with a solvent to remove certain undesirable constituents, and distilling off the solvent.

High-boiling fractions from pitches and tars, together with the second anthracene fraction obtained in pitch rectification (softening temperatures 69° to 85° C, 19 to 33 percent insoluble in toluene, and 71 to 77 percent volatile) show promise as bonding agents for coal briquets.\textsuperscript{132} Average softening temperatures of such pitches rose from 79° to 101° C during 12 months, while the volatile contents dropped slightly, from 73.3 to 71.4 percent. Briquets bonded with 12 percent of pitch at 150° C and pressed at 95° C and 400 kg/sq cm possessed high mechanical and water resistance and were not tacky.
A German patent specifies a mixture of hot pitch, dispersible clay, water separated during the purification of gas, and 0.5 to 4 percent naphthalene, anthracene, or phenanthrene, as a suitable binder to be trituted with coal in making briquets.

Another patent describes the briquetting of wet coal sludge by mixing it with 5 percent of a liquid pitch-coal product obtained by heating fluxed hard pitch and powdered coal up to 300° C.

The use of wash oil or lignite tar oil and pitch in briquetting solid fuels is claimed in another German patent. Still another applies to the use of tar-pitch melts as binders for fuels that are not easily coked, and are moist and fine grained.

Lignite pitch as a binder for the briquetting of crushed solid fuels is specified in another German patent.

A discussion of the optimum properties of pitches, the addition of 20 to 30 percent pitch distillate to promote better covering of the coal particles, the use of pitch emulsions and of air-blown pitch distillate has been published. Laboratory experiments have shown it possible to prepare satisfactory briquets by adding 8 percent or more of coal tar residue with a melting point of 95° C to coal fines.

A German patent describes the use of tars and pitches from the low-temperature carbonization of brown coal as binders for briquetting coal and other solid carbonaceous fuels.

The influence of the chemical and physical properties of pitch on its binding characteristics has been studied, with special attention to the role of the α, β, and γ constituents. (Note: the α fraction is that portion insoluble in pyridine; the β fraction is soluble in pyridine but insoluble in chloroform; and the γ fraction is soluble in both pyridine and chloroform-G.R.Y.) The content of the β and γ components should be about 80 percent and their ratio 1:1. Low-quality pitch contains high amounts of α and γ components. In this study, the ductility of the pitch was stressed.

A technique has been developed whereby the pitch binder in a coal briquet can be made visible and the amount used can be estimated by microscopic examination.

A study of medium-soft pitches from coke oven, horizontal retort, vertical retort, and low-temperature tars has been made, using infrared analyses, solvent extraction, and chemical analyses. Physical properties were related to viscosity, and specifications for pitch as a binder for briquets and carbon electrodes were reviewed.

A further study of binders by a viscosity measurement (the torque required to rotate a platinum disc dipped into the molten sample) at temperatures between 40° and 140° C has included hard pitches. Agglomerating properties were evaluated by determining the compression strengths of pitch-coke briquets made with the binders. Values obtained with the pitches were about as might be expected on the basis of industrial experience.
Various additives have been used with pitches in the preparation of binders. A U. S. patent relating to the making of carbon or graphite electrodes specifies the use of less than 5 percent of an additive with pitch, or with a tar which is subsequently distilled until an 80° C softening point is attained. Suitable additives listed are MnCl₂, CrCl₃, FeCl₃, nitrobenzene sulfonyl chloride, p-toluene sulfonyl chloride, or nitronaphthalene sulfonyl chloride.

A Japanese patent mentions the use of coal-tar pitch and resin in fish oil or mineral oil, dispersed by means of an alkaline solution of cellulose, as a briquet binder.

Making refractories of calcined dolomite and a binder of 65 to 70 percent coal-tar pitch and 30 to 35 percent anthracene oil and pressing at more than 500 kg/sq cm has been described.

A German patent describes bonding carbon articles together or to metals with a mixture made up of one-third pitch, one-third electrode graphite, and one-third graphitic acid.

A German patent involves mixing tar oils and wood or lignin with pitch to obtain binders with a wide plasticity range. For example, 1000 kg of tar pitch was heated until the softening point rose to above 100° C, and then 850 kg of anthracene oil and 300 kg of lignin were added. Heating was continued 3 to 4 hours to decrease the point of fracture.

Hard spherical coal pellets for subsequent activation with steam at 1750° F were described in a U. S. patent; they were made by mixing the pulverized coal with 20 to 30 parts of core pitch and tumbling the pellets with 40 cc per 100 g of powder of a molasses solution of specific gravity 1.10 to 1.15.

A German patent describes the use of an emulsion or suspension of pitch, prepared with the aid of such an emulsifying agent as concentrated sulfate liquor, as a binder for briquetting carbonaceous fuels; a Japanese patent claims what appears to be a similar mixture made up of 25.5 parts of coal tar, 48.3 parts of coal tar pitch, 25.4 parts of water, 5 parts of 30° Be waste pulp liquor, and 0.1 part of NaOH mixed together at 95° C.

POLYACRYLAMIDE

Polyacrylamide is a water-soluble, nonionic powder made by the polymerization of acrylamide. In aqueous solutions it is compatible with most natural and synthetic water-soluble gums, latex systems, and many salts; it is a good thickening agent, protective colloid, and binder.

POLYALKYLENE GLYCOL-POLYETHYLENE OXIDE

The binding of precious-stone abrasives with a polyalkylene glycol-ethylene oxide polymer is described in a U. S. patent. For example, 20 g of diamond or sapphire powder was dispersed with 54 g of polyalkylene glycol and agitated while 26 g of ethylene oxide was added; heating and stirring were continued until a uniform consistency was obtained. The polymer had a molecular weight of 4000 and melted at 50° C.
POLYAMIDES

Magnetic cores, described in a French patent,\textsuperscript{155} were made by emulsifying a superpolyamide with 80 percent ethanol in an autoclave at 1 kg/sq cm pressure and 120° C, mixing with a magnetic powder such as iron, homogenizing in a heated mixer, coagulating with cold water, and homogenizing again.

POLYESTER RESINS

A U. S. patent\textsuperscript{156} describes a binder that may be used for abrasives and other materials. A mixture of 4.4 parts of ethylene glycol, 44.7 parts of commercial pentaerythritol, 21.5 parts of a diallyl ether mixture of pentaerythritol, 22.34 parts of maleic anhydride, 2.3 parts of boric acid, and 18.6 parts of water was heated under CO\textsubscript{2} and stirred at 170° to 190° C for 3 hours. The product had an acid number of 17.4; it was diluted with water to 75 percent solids prior to use.

POLYMERS OF HYDROCARBONS

A Dutch patent\textsuperscript{157} describes the use of various polymers and/or copolymers of olefinic hydrocarbons, their mixtures, and their mixtures with pitch. Monomers listed as suitable starting materials are ethene, propene, butene, butadiene, and styrene. The binders were used in making fuel briquets.

POLYURETHANES

A U. S. patent\textsuperscript{158} gives the details of preparing elastic grinding articles. In an example, 600 g of Al\textsubscript{2}O\textsubscript{3} was moistened with a solution of 10 percent of 4,4',4"-tri-isocyanatotriphenylmethane in CH\textsubscript{2}Cl\textsubscript{2}, the solvent evaporated and the Al\textsubscript{2}O\textsubscript{3} added to a molten, castable polyurethane polymer, stirred vigorously for 30 seconds, and the mixture placed in molds for 24 hours. The polyurethane was prepared by adding 70 g of 1,4-butandiol to the reaction product of 1000 g of linear polyesters containing aliphatic OH groups and 300 g of 1,5-naphthalene diisocyanate and stirring for 30 seconds.

POLYVINYL ACETAL

A bonding composition for magnetic metal described in a U. S. patent\textsuperscript{159} consists of 42.5 percent of polyvinyl acetal (obtained by the reaction of 70 percent hydrolyzed polyvinyl acetate with acetaldehyde), 42.5 percent of polyvinyl acetate, and 15 percent of a B-stage condensate of cresylic acid and formaldehyde.

PRICKLY PEAR LATEX

A latex can be obtained by pressing prickly pears; when mixed with sulfur and heated under pressure this forms a binder. It is not water-resistant.\textsuperscript{160}
RESINS

The use of synthetic resins as binders for magnetic granules has been described,\(^{161}\) and a German patent\(^ {162}\) deals with the use of such resins in binding fuel briquets.

Another German patent\(^ {163}\) describes water-resistant binders, useful for abrasives, which were made from novolak-hexamethylenamine and coal tar pitch that had been modified by blowing.

SAWDUST

An Austrian patent\(^ {164}\) claims that briquets can be made from coal which alone is not amenable to briquetting (e.g., brown coals) by mixing it with 20 to 50 percent of sawdust or similar wood waste and pressing at 1200 to 3000 atmospheres.

SHALE BITUMEN

Heating Baltic shales up to about 380\(^\circ\) C converts much of their organic matter to an extractable form, called pyrobitumens. These pyrobitumens showed good binding properties when used for the briquetting of fine coal.\(^ {165}\)

SHELLAC

The use of shellac for binding abrasive articles has been patented in the United States.\(^ {166}\)

SOYBEANS (See Lupines and reference 113.)

STARCH

Various starch preparations, derivatives, and mixtures have found numerous applications as binding agents. As a binder for fuel briquets, a U. S. patent\(^ {167}\) claims a solution of 100 grams of potato starch dextrin in 1 liter of water which was heated while 100 ml of glacial acetic acid was added. Other organic acids may also be used. A rather similar procedure is given in a Dutch patent,\(^ {168}\) which claims that this binder permits the use of much lower pressures for briquetting than those permitted by pitch binders.

Another U. S. patent\(^ {169}\) gives a process that calls for further additives. Twenty kg of potato starch was mixed gradually with 2.7 kg of 80 percent acetic acid and the mixture heated to 175\(^\circ\) C. A mixture of 2 kg of polyvinyl acetate and 2.5 kg of 80 percent acetic acid heated to about 60\(^\circ\) C was added to the first mixture, and 0.6 kg of paraffin also was added. This mixture was carefully and thoroughly mixed with 1000 kg of coal dust containing 11 percent H\(_2\)O, the temperature raised to 90\(^\circ\) C by steam injection, and the briquets pressed and air dried. They were resistant to outdoor storage and did not disintegrate during burning.
The use of starch in the presence of alkalis also has been applied to making fuel briquets. A British patent\textsuperscript{170} dealing with the making of briquets from peat that had been treated with alkali does not, however, claim the starch as a binder, but says that a small quantity of starch is incorporated before, during, or after the alkali treatment in amount insufficient to act as a binder but sufficient to replace the lost colloidal substances of the peat.

Another British patent\textsuperscript{171} says that a binder for fuel briquets was prepared by mixing starch, water, and an alkali such as Na\textsubscript{2}CO\textsubscript{3} or NaOH and heating the mixture to 220° to 350° F to produce a heavy, viscous, sticky fluid. A U. S. patent\textsuperscript{172} claims the production of a material suitable for use as an adhesive or a binding agent from potato starch, sodium chloroacetate, and barium hydroxide.

A Belgian patent\textsuperscript{173} specifies as a binder a product obtained by esterifying starch at 60° to 300° C with 1 to 20 percent of an inorganic acid in the presence of 5 to 50 percent of urea and treating it with 5 to 50 percent of an aldehyde at a pH of 6 to 9. Curing may be done at 20° to 200° C.

A U. S. patent\textsuperscript{174} describes the preparation of a binder for various materials. Five hundred parts by volume of a 40 percent solution of formaldehyde was diluted with an equal volume of water containing 20 parts by volume of 80 percent acetic acid; 500 parts by weight of potato starch was suspended therein and the mixture maintained at room temperature several hours prior to use.

**STYRENE POLYMERS**

A German patent already cited\textsuperscript{45} (see Glycerol) mentions the use of polystyrene.

A copolymer of styrene and linseed oil is described in another German patent\textsuperscript{175} as a suitable binder for coating formulations. A mixture of 900 g of styrene, 18 g of di-tertiary butyl peroxide, and 1.8 g of sulfurized dipentene was added over a period of 2 hours to 1100 g of stirred linseed oil at 180° to 200° C. The sulfurized dipentene was obtained by heating 100 g of dipentene and 5 g of sulfur at 150° to 250° C.

**SULFITE LIQUOR**

The reclamation of dust from the abrasion of lignite briquets is the subject of an East German patent.\textsuperscript{176} The dust was mixed with 2 to 5 percent sulfite waste liquor (31° Bé) at 50° C and processed on a conventional extruder. The resulting briquets had strengths up to 80 kg/sq cm.

Low-temperature carbonization of coal briquets for which 4 to 6 percent of beech wood sulfite liquor or 1.9 to 3 percent cassava flour was used as the binder has been described.\textsuperscript{177}

A Russian patent\textsuperscript{178} on the briquetting of coal describes a binder consisting of sulfite liquor and 3 to 5 percent of oxidized petrolatum, and a German patent\textsuperscript{179} claims the use of sulfite liquors added to the fuel before
or simultaneously with a tar-pitch melt to give briquets that may be rendered weather-resistant by heating at 150° to 200° C.

TAR

Tars of various kinds, like bitumens and pitches, find many applications as binders. Often there is no clear-cut distinction between these materials.

In one study, a horizontal retort tar was brushed on various test pieces of rock. After an hour these were immersed in Na₂CO₃ solutions of known concentrations. The concentration of Na₂CO₃ required to strip the tar from the test piece in 24 hours at room temperature was a measure of the adhesion. The following qualitative estimates of adhesion to each rock type are given: orthoclase - bad; hornblende - bad; biotite - poor; quartz - poor; labradorite - poor; augite - good; olivine - excellent.

Low-temperature tars from peat and brown coal generators, low in aromatics content, were blown with oxygen at 200° C for 2 to 7 hours to raise the softening points; when used in amounts up to 7 percent of the dry fuel they were satisfactory binders for briquetting bituminous and anthracitic coal fines.

A wide variety of tars and tar mixtures was studied in a search for binders for anthracite fines. These included petroleum residues, hydrogenation residues, coal tar, generator tar, wood tar, and others; over 100 experiments were carried out.

A German patent describes the modification of tar by heating it to 150° to 350° C with oxygen-producing substances that leave no undesirable impurities, e.g., (NH₄)₂S₂O₈ (ammonium peroxydisulfate) or activated carbon, prior to use as a binder for coal. This treatment is claimed to increase the content of pyridine- and benzene-soluble components and thus increase the adhesive power of the tar.

A review of the physical and chemical properties of tars and pitches and their effects on binder performance has been published.

A study of the effects of water in tar binders has shown that binder consumption may be reduced by determining the optimum water content, by lowering the surface tension of the water by adding such agents as benzyl alcohol or soap, and by using water-tar emulsions.

A Japanese patent claims good binding properties (for fuel briquets) for a binder consisting of an emulsion of 50 percent of a mixture of 1 part minus 60 mesh coal and 4 parts coal tar heated 2 hours at 300° C, 15 percent coal tar, 8 percent 30° Bé waste pulp liquor, and 27 percent water, mixed and applied at 90° C.

Tar mixtures, useful in binding rock aggregate such as that used in road building, are specified in a French patent as 40 to 45 parts of tar and 60 to 45 parts of a 300° to 360° C anthracene oil fraction.
Lime-treated tars are used in making binders for road surfacing materials and for briquetting some coals, and a study of the physical changes that accompany the addition of the lime has been published. Making calcium carbide briquets with 20 to 23 percent of a binder containing 45 percent coal tar and 55 percent coal tar pitch is more satisfactory than using pitch alone.

The use of wood tar from wood chemical plants as a binder for making charcoal briquets has been described. The charcoal and wood tar were ground together, heated to 110° to 120° C, pressed at 65 to 300 kg/sq cm, and baked at 420° to 450° C for 35 to 40 minutes.

TARTRATES

In using chromium compounds in the binding of dead-burned magnesite, a strong, dense, crack-free mass is obtained by adding 0.25 to 2.5 percent of an alkali metal tartrate and firing the mixture at 2800° to 2910° F. (See also Chromium Compounds under Inorganic Binders, and reference 16.)

UREA-FORMALDEHYDE RESINS

Modified urea-formaldehyde or phenol-formaldehyde resins with improved bonding strength characteristics are produced by making a precondensate with a predetermined methylol content and treating it with a mixture of furfural and furfuryl alcohol in the monomeric or semipolymerized state. The viscous resin so obtained is useful in making abrasive articles.

VINYL POLYMERS (See also Glycerol, reference 45; Glycol Ester Derivatives, reference 108.)

A U. S. patent deals with the use of latex materials for binding abrasives. These latexes were made by the emulsion polymerization of a vinyl chloride-vinylidene chloride mixture, or a styrene-butadiene mixture. One latex, for example, contained 75 percent vinyl chloride and 25 percent vinylidene chloride. The latex was added to the grit, such as SiC, mixed, and the water evaporated to leave free-flowing granules that were then placed in molds, pressed, and heated at 600° C for 36 hours to form the abrasive articles.

A French patent specifies the bonding of abrasives with one or more polymerized vinyl compounds that contain sufficient OH groups to be soluble or dispersible in water. This may be a polyvinyl alcohol, a partly hydrolyzed polyvinyl compound, or a polymerized vinyl ester of a hydroxy acid.

ZÄHLIT

Zählit-D is an unsaturated hydrocarbon fraction with a specific gravity about 1 and Engler viscosity of 1300° at 50° C and 12.5° at 125° C. It is used, according to a Belgian patent, as a binder for mineral fibers, for mica and asbestos to form insulators, or for lead salts to form bricks for radiation protection.
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