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## FIRE-RETARDANT COMPOSITION CONTAINING AN ANION EXCHANGE RESIN

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14 Claims. (Cl. 260-15)

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This invention relates to the improvement of the fire and heat resistance of materials and is more particularly concerned with fire-retardant and potentially heat-insulating nitrogen-containing resinous compositions. The invention also relates to methods of employing these compositions, and of processing materials to impart thereto fire and heat resistance. The invention further comprises the products obtained by such processing.

The most efficient fire-retarding compositions of the prior art usually contain inorganic fire-retarding compounds which are admixed, in some cases, with various organic materials. The inorganic fire-retardants retain in these compositions their inherent physical and chemical characteristics such as acidity or alkalinity, crystallinity, and others, which greatly limit the usefulness of these compositions.

For example, strong inorganic acids, in particular phosphoric acids, are good fire retardants, but compositions containing the free acids in any appreciable amount are water-soluble, do not dry satisfactorily and usually impair materials to which they are applied; and salts of phosphoric acid, in particular ammonium phosphate, render the compositions water-soluble, and in many cases hard and brittle.

The fire-retarding compositions of the prior art may be divided into two classes: the first comprises compositions in which at least one of the ingredients essential in providing fire-retardance is water-soluble; the second class comprises water-insoluble compositions. To the first class belong the compositions based on alkali silicates, and the compositions comprising inorganic water-soluble fireproofing compounds such as inorganic acids and salts, especially alkali and ammonium phosphates, sulfates, sulfamates, borates, halides, etc. To the second class belong compositions which contain water-insoluble inorganic fire-proofing compounds such as antimony oxide and heavy metal stannates, and compositions containing organic materials such as chlorinated rubber, chlorinated paraffins and similar chlorinated organic materials.

It is well-known that the best water-soluble compositions are considerably more effective in fire-retardance than the best water-insoluble compositions. For example, compositions in

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which a soluble inorganic compound such as ammonium phosphate, ammonium sulfate, etc., is mixed with a urea-formaldehyde resin and preferably with a carbohydrate, when exposed to heat, form a carbonaceous foam of outstanding fire-retarding and heat-insulating properties. This type of composition is far superior in fire-retarding qualities to any of the other compositions but it lacks water-resistance and it is somewhat brittle because of the crystalline character of the inorganic salts used.

If both water-resistance and good flexibility are desired, the alternatives suggested by the prior art therefore are compositions containing chlorinated paraffins and the like, and insoluble compounds such as heavy metal stannates or antimony oxides. But these compositions are very inferior in fire resistance. They are not potential heat insulators and are therefore entirely unsuitable for protecting non-combustible materials, such as metal, from damage by heat. They are unsuitable for use with wood, insulating board, etc., because they are not effective enough to impart a sufficient measure of fire-retardance to such materials. Their main use is on fabrics, but even there they require heavy impregnations to pass fire tests. Finally, they are quite expensive.

An object of this invention is to provide improved fire-retardant resinous compositions having none of the undesirable physical and chemical characteristics inherent in inorganic fire-retarding compounds but at the same time having superior fire-retardant and potential heat-insulating properties.

Another object of the invention is to provide improved methods of processing materials to impart the properties of fire and heat resistance thereto.

Another object of the invention is to provide coated or impregnated products having enhanced fire and heat resistance.

Another object of the invention is to provide improved products consisting mainly of normally combustible materials but which have improved fire resistant properties.

In general we have discovered that reaction products of basic nitrogen-containing anion-exchange or acid-adsorbent resins with non-oxidizing inorganic acids, which reaction prod-



ucts will hereinafter be called "resin salts," are substantially less inflammable than the basic resins themselves and are capable of forming a fire-retardant and heat-insulating carbonaceous mass when subjected to elevated temperatures, for example, of the order of temperatures of flaming wood, wall board and the like, burning in air. By "non-oxidizing" acids we mean the monovalent hydrogen halides and the polyvalent acids; by so defining and limiting the term "non-oxidizing" in this specification and in the appended claims we disclaim those acids, particularly nitric acid, chloric acid, perchloric acid and the like, which are such strong oxidants that they tend to increase rather than reduce the combustibility of the basic resin. As basic resins we may use condensation products of amines or other organic bases with aldehydes, phenols or other condensing agents, as more fully described below.

To form resin salts which are stable towards leaching, we prefer to use strong non-oxidizing inorganic acids having a dissociation constant of  $10^{-3}$  or higher. As used herein, the term "acid" includes acid salts. We have found that the divalent acids form more stable resin salts than the univalent acids, and that the tri- and tetravalent acids form resin salts of even better stability than the divalent acids. While hydrochloric acid, and hydrobromic acid, for example, form, with the basic resin, resin salts of reduced inflammability which are effective fire-retardants to a greater or less extent, and sulfuric acid forms resin salts somewhat better in this respect, we have found that phosphoric acids yield resin salts with the basic resins which are much superior. They are substantially non-inflammable at flame temperatures of, say,  $750^{\circ}\text{C}$ . or less, and possess excellent fire-retarding and potentially heat-insulating properties yielding on exposure to flame temperatures a carbonaceous, heat-insulating mass which is resistant to combustion. These resin salts are highly stable; in some instances they resist not only leaching by water and by mono- or divalent acids, but even by alkalis and by organic solvents.

As the amount of acid combined per gram of basic resin is increased, the effectiveness of the product increases. Thus we have found generally that not less than one milliequivalent and preferably at least two milliequivalents of acid per gram of basic resin is required to make a product of practical value. Consequently, while the reaction products of the basic resins with strong non-oxidizing inorganic acids in general possess reduced inflammability and are suitable fire-retardants for some purposes, we prefer those reaction products of basic nitrogen-containing resins with phosphoric acids, which contain at least two milliequivalents of phosphoric acid per gram of basic resin. Usually, but not necessarily, the basic resins do not combine with more than 15 milliequivalents of phosphoric acid per gram of basic resin.

We have found that combustible materials such as wallboard, fibreboard, cardboard, wood including plywood, fabrics, paper, etc., can be rendered less inflammable or substantially fire-proofed by coating and/or impregnating them with the resin salt. The treatment can be carried out, for example, by first dispersing the insoluble, heat-cured, finely divided resin salt in a liquid vehicle containing a film-forming bonding agent such as a drying oil, an alkyd or other film-forming resin, a cellulose derivative, for ex-

ample ethyl cellulose, methyl cellulose, cellulose acetate, and the like; then applying said dispersion to the combustible material by painting, spraying, or other suitable means and then drying the treated material until a solid fire-retardant film is formed on the treated material. The combustible material can also be treated by applying the resin salts in an early stage of their manufacture. For example, the resin forming ingredients may be reacted in water in the presence of the strong non-oxidizing inorganic acid, the combustible material may be treated with the aqueous solution or dispersion of the resin salt in a low state of polymerization in which it is still capable of remaining dissolved or suspended as a colloid, and in which state the resin salt possesses good bonding and film-forming properties, and the treated material may then be heat-cured. In general there is formed by this treatment a protective fire-retardant solid film on the combustible materials. In the case of fabrics, paper, wood, or other porous combustible materials, the aqueous solution or dispersion of the resin salt may also be used as an impregnating liquid. When so used the fire retardant resin salt is deposited in and on the combustible porous material which is thereby impregnated. Use as a fire-retardant adhesive may also be made of the resin salt in a low state of polymerization to glue paper, veneer or other laminated materials to a surface. In this case the paper or the like and, if desired, the surface to which it is to be glued, are treated with the aqueous dispersion of the resin salt as above, the two surfaces are pressed together and the film between the surfaces is cured as, for example, by heating. When so used the bonding properties of the aqueous resin salt dispersion may be enhanced by adding to the dispersion a conventional bonding agent such as wheat paste and the like. We have also found that incombustible materials, particularly metals, may advantageously be coated with resin salts by the same methods of application, whereby use is made of the potentially heat-insulating properties of the coating for protecting the metal from damage by heat or for reducing the heat transmission through it when exposed to flame temperatures.

It should be noted that the term "acid adsorbent" is somewhat misleading because the basic resins do not merely adsorb acids but appear actually to react chemically with the acids. In fact, the mechanism of acid adsorption is probably mainly that of chemical reaction with some characteristics of adsorption. Consequently when the term "acid adsorbent" is used in this specification, it is understood that it includes a chemical reaction. Furthermore, we use the terms "acid-adsorbent resin" and "anion-exchange resin" interchangeably in this specification and in the claims. We wish it understood that the resins so designated are intended to include basic resins capable of forming resin salts from which the acid is no longer completely removable by treatment with an alkali or another acid.

It is well known that in recent years many synthetic resinous anion-exchangers have been prepared and are being used mainly for water purification. The preparation and use of these resins in water purification and allied fields has been described in detail in the chemical literature. For example, reference is made to United States Patents Nos. 2,151,883, 2,198,874, 2,246,527, 2,251,234, 2,259,169, 2,290,345, 2,341,907, 2,354,671,



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2,356,151 and 2,36,086. Acid-adsorbent resins are obtained in general when basic nitrogen-containing organic compounds such as amines, or guanidine, and the like, are condensed with aldehydes, hydroxy aldehydes (sugars, starch, etc.), or with mixtures of aldehydes and ketones, under such conditions that not all of the basic groups are linked to aldehyde residues in the formation of the resinous structure; that is, only resins containing free basic groups exhibit anion-exchanging properties. Typical acid-adsorbent or anion-exchange resins suitable for the formation of fire-retardant and potentially heat-insulating compositions with strong inorganic acids include the following classes:

Resins made by condensing

(1) meta-substituted aromatic amines or aromatic polyamines with aldehydes and/or carbohydrates with or without ketones;

(2) aliphatic polyalkylene polyamines with aldehydes and ketones;

(3) aliphatic polyalkylene polyamines with phenols and aldehydes;

(4) a strongly basic derivative of cyanamide, with a weakly basic derivative of cyanamide, and with an aldehyde, as more fully defined below. In addition, a carbohydrate may be included.

As aldehydes we use aliphatic aldehydes, particularly formaldehyde or a source of formaldehyde such as paraformaldehyde, trioxymethylene and the like, acetaldehyde; or cyclic aldehydes such as furfural and the like. Carbohydrates (sugar, starch, etc.), which are mentioned specifically whenever they may be used and which may or may not contain aldehyde ( $-\text{CHO}$ ) groups, are not necessarily equivalents of aldehydes in forming fire-retardant resin salts.

A great variety of operative anion-exchange resins or resinous mixtures may be prepared by varying the above components, or by co-condensing them with other resin forming ingredients; for example, anion exchangers may be formed in which strongly basic quaternary ammonium hydroxides are used in place of, or in addition to, an organic amine or guanidine or the like; or hydroxy aldehydes and hydroxyketones, in particular carbohydrates (sugar, starch, etc.) may be used in addition to, or in place of, the aldehydes of the components of classes 2 and 3; or amines may be reacted with a derivative of a polyvalent organic acid and with an aldehyde (for example an aminoalkyl-malonamide,  $\text{ROOC}-\text{CH}_2-\text{CONH}(\text{CH}_2)_n\text{NH}_2$ , resulting from the reaction of an aliphatic polyamine with a malonic ester, may be condensed with formaldehyde). It is evident to anyone skilled in the art that these and other variations may be made without departing from the scope of this invention.

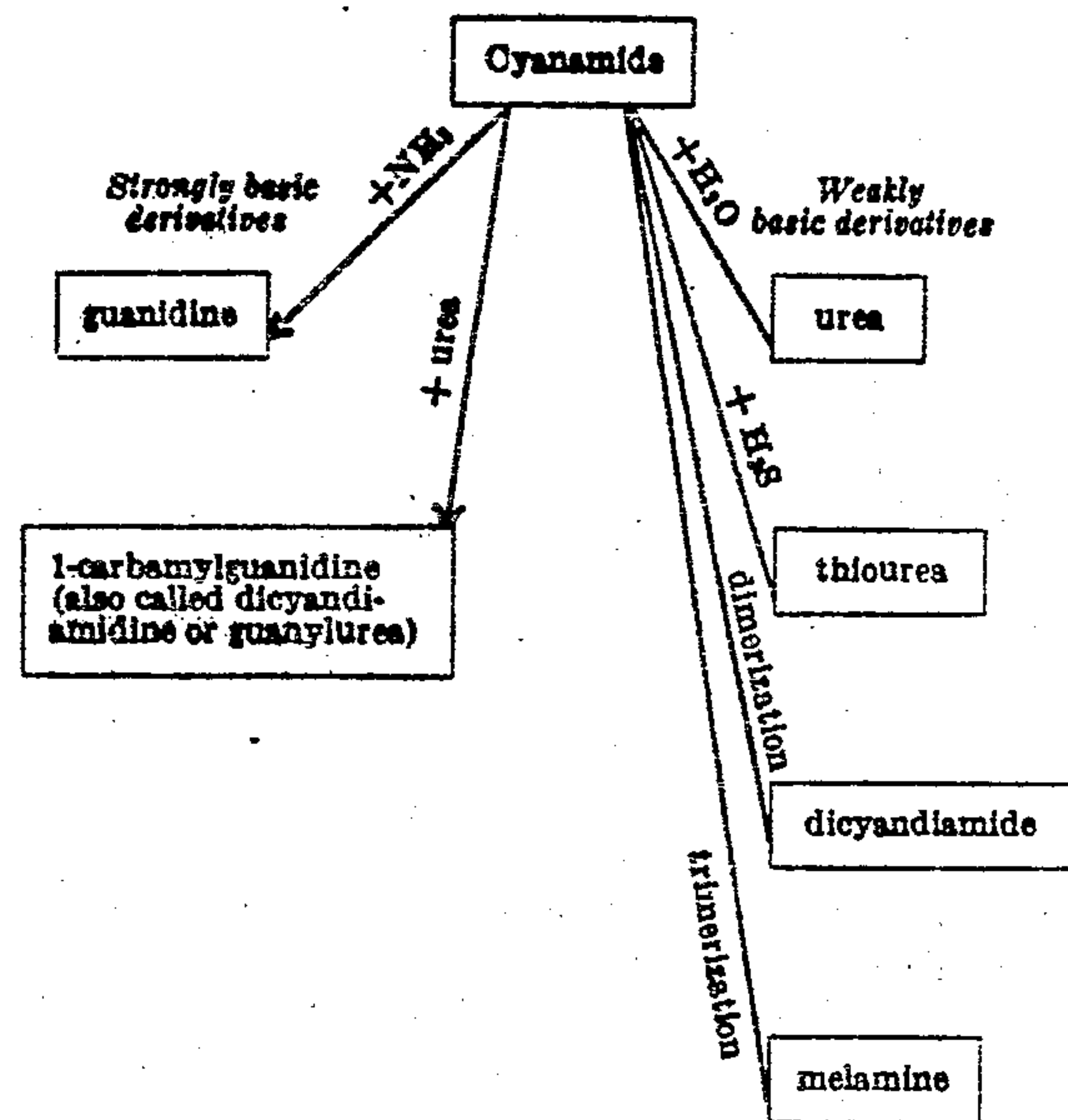
Preferably the resins are combined with as large an amount of acid as possible. In general, resins of the above types will combine with 1 to about 15 milliequivalents of acid per gram of resin. In some cases it is possible to use considerably more acid, for example, as much as 25 milliequivalents or more per gram of resin.

While we have found that the anion-exchange and acid-adsorbent resins in general are suitable for the preparation of fire-retardant resin salts, we have found that the resins of class (4) form more stable resin salts which are generally better fire-retardants. In this preferred class of resins we find it necessary to use an aldehyde as one of the resin-forming agents. While it is possible to use a carbohydrate in addition to the aldehyde,

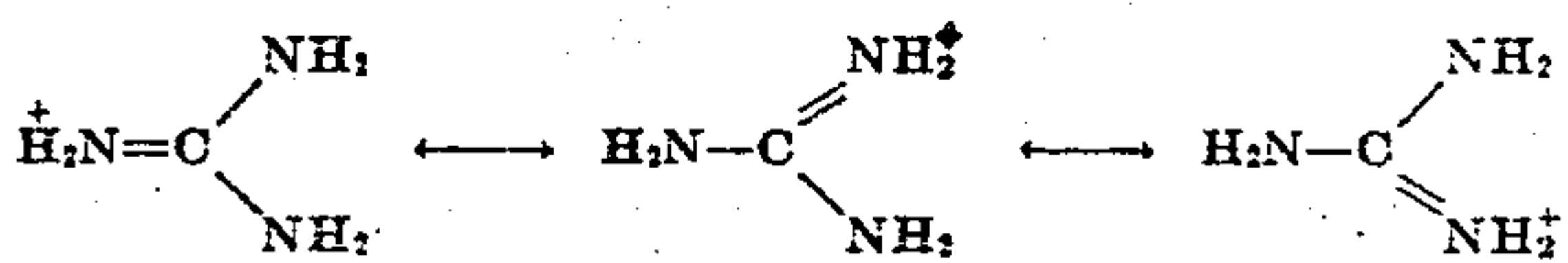
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we cannot use a carbohydrate in place of the aldehyde because the resulting mixture containing no aldehyde is no longer a fire-retardant resin salt as defined herein; it tends to crystallize, thereby losing its resinous characteristics to a large extent, and possesses inferior water resistance.

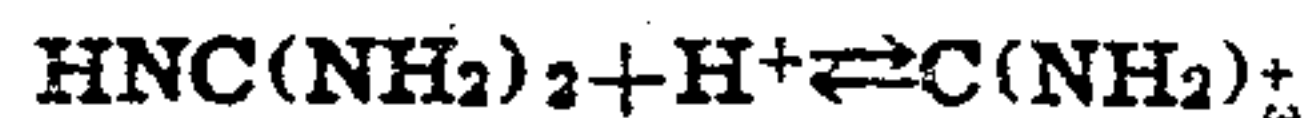
This preferred class of resins comprises co-condensation products of a strongly basic derivative of cyanamide and of a weakly basic derivative of cyanamide, with an aldehyde. Cyanamide has the formula  $\text{CN}_2\text{H}_2$  and its structure may be written  $\text{N}\equiv\text{C}-\text{NH}_2$  or  $\text{HN}=\text{C}=\text{NH}$ . Some of the more important derivatives of cyanamide which may be used according to this invention are shown in the following diagram:



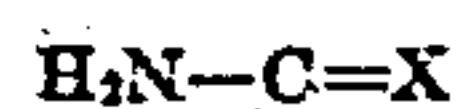
The strongly basic character of guanidine is generally attributed to the fact that the guanidinium ion  $\text{C}(\text{NH}_2)_3^+$  resonates between three equivalent structures



The resonance energy of these three structures makes the guanidinium ion more stable than guanidine itself, thereby favoring the right side of the equilibrium



Derivatives of guanidine for which two equivalent structures for the corresponding ion can be written, though somewhat less basic, are usually still strong bases. For the purpose of forming the preferred co-condensation products of class (4), we chose a strongly basic derivative of cyanamide, that is, guanidine or an equivalent thereof as defined below, which will give basic "spots" in the resinous structures having two equivalent resonating structural groups. The weakly basic derivative of cyanamide used to form the preferred co-condensation products is chosen to contain the group



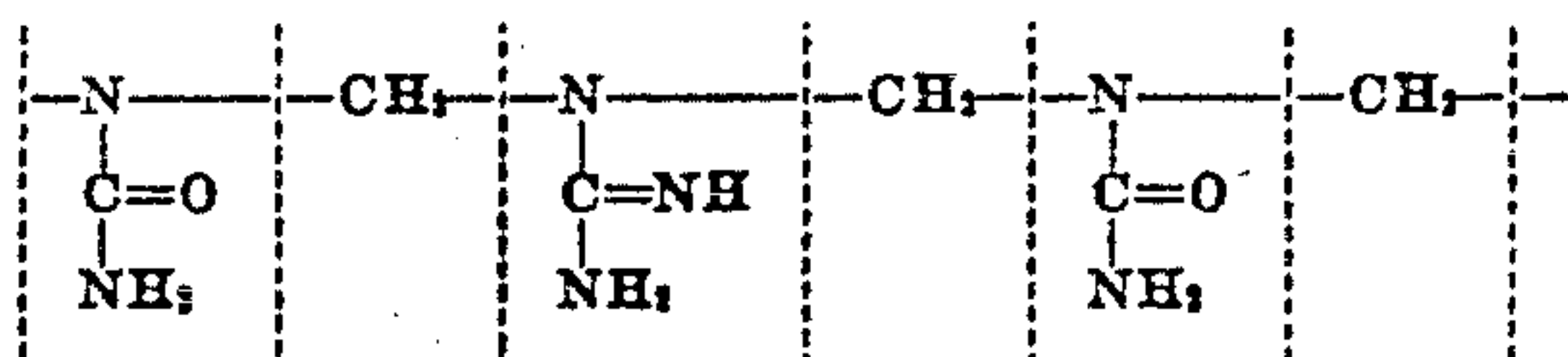
where X may be O, S, NH or N—, this group



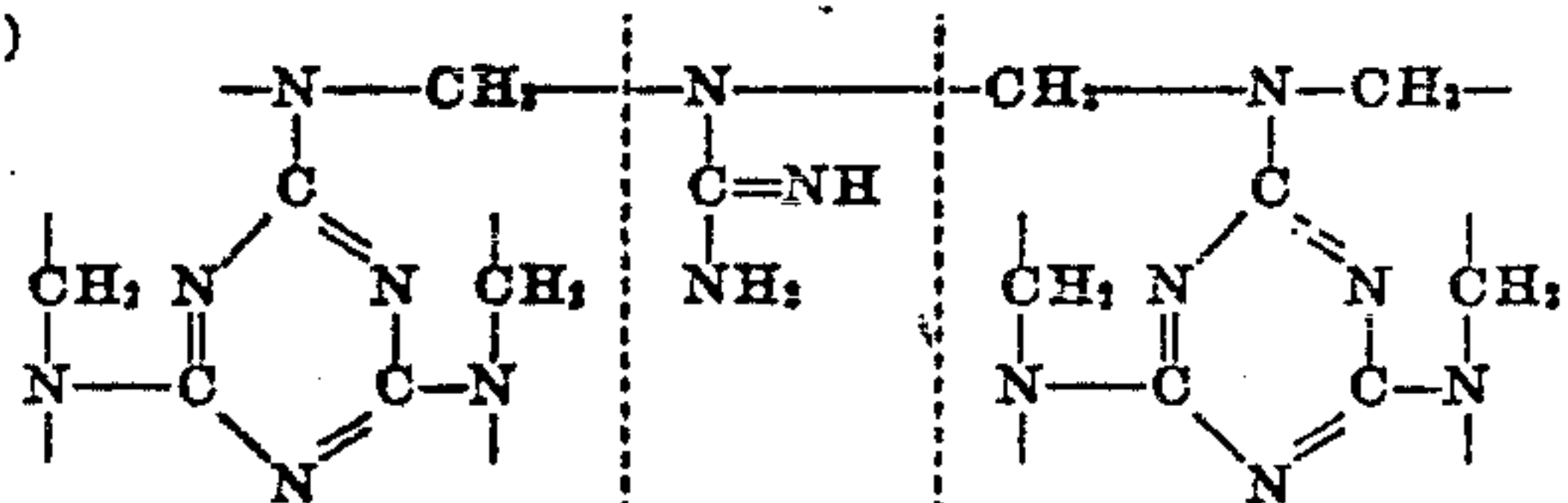
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being capable of reacting with aldehydes to form resins. It should be noted that the strongly basic derivative of cyanamide contains, in addition to the basic resonating structures, this same aldehyde-reactive group. While we do not limit ourselves to any particular theory, we believe that typical resinous co-condensation structures of the preferred class (4) may be illustrated by the plausible structural Formula I for a product made from guanidine, urea and formaldehyde, and II for a product made from guanidine, melamine and formaldehyde:

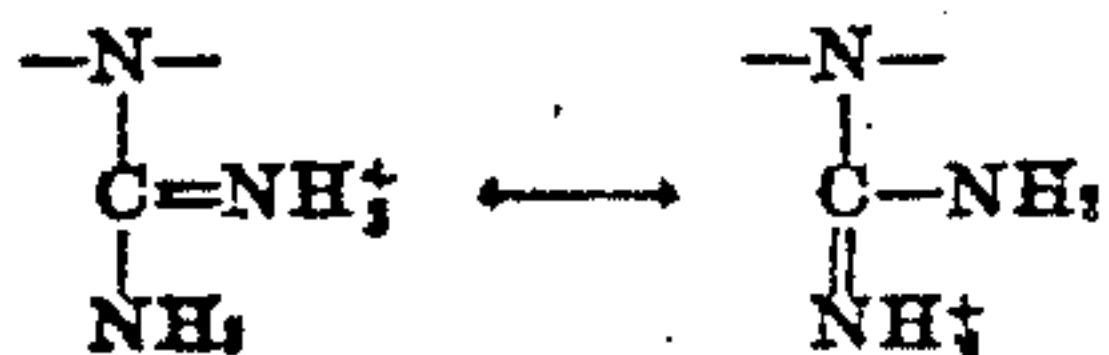
(I)



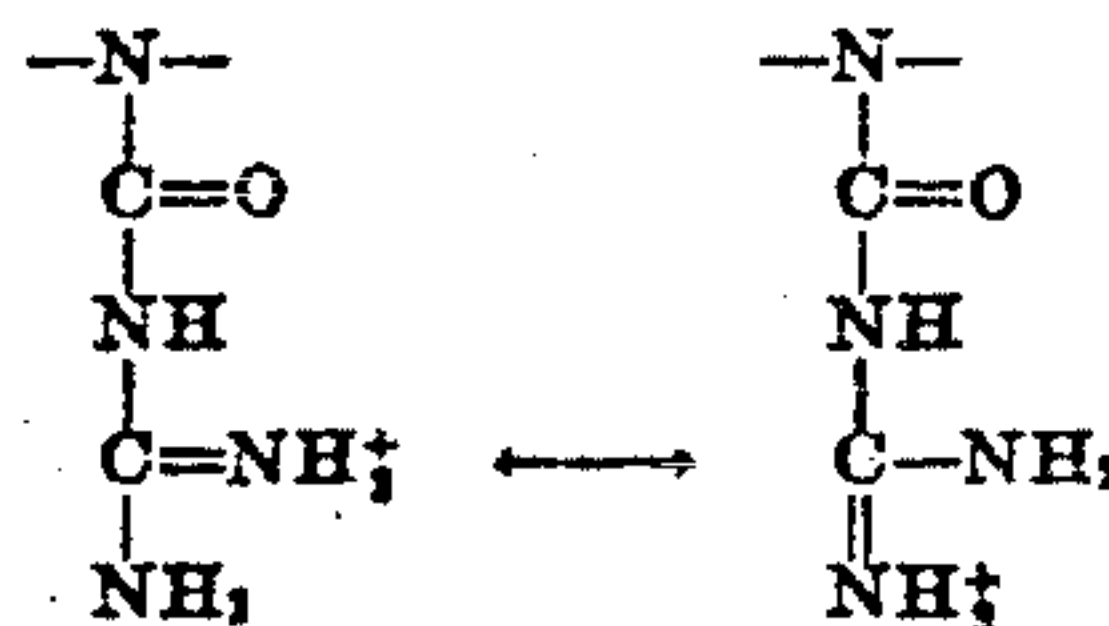
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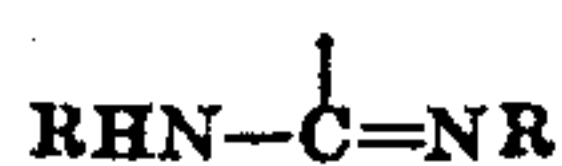
It will be noted that in these structures the guanidine segment can resonate, when attracting a hydrogen ion, between the two equivalent structures:



In a similar co-condensation structure 1-carbamylguanidine (also called dicyandiamide or guanylurea) gives an acid adsorbent segment which when reacted with  $\text{H}^+$  may be written



Thus, in general, as strongly basic derivatives of cyanamide, we may use compounds which will give, when condensed with an aldehyde and with a weakly basic derivative of cyanamide, an acid adsorbent resinous structure containing the group



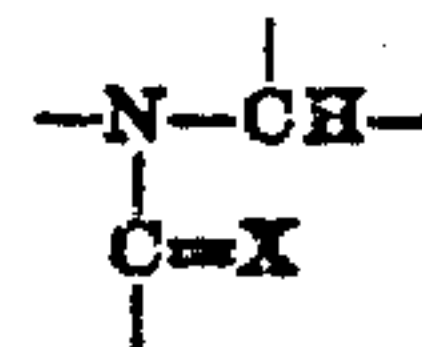
where R may be H,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or the like alkyl group. This group of strongly basic compounds, which is termed strongly basic derivatives of cyanamide in this specification and the appended claims, includes guanidine, 1-carbamylguanidine, and the like. As weakly basic derivatives of cyanamide we may use in general compounds containing the reactive group



where X may be an oxygen atom, a sulfur atom, an NH group or N—. This group of weakly basic compounds which is termed weakly basic derivatives of cyanamide in this specification and the appended claims includes urea, thiourea, dicyan-

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diamide, melamine and the like, that is in general compounds containing the said reactive group which will form, with an aldehyde, in the resinous structure, the segment



The preferred resins of class (4) usually have a higher nitrogen content than the resins of the other three classes; we believe that this high nitrogen content contributes to reduction of the combustibility of the basic resin itself, and, in conjunction with the inorganic acid, tends to make a resin salt which forms a more voluminous and less combustible carbonaceous mass on exposure to flames.

The fire-retardant and potentially heat-insulating resin-salt when heat-cured, is a solid substantially water-insoluble product which is very different in chemical nature from the mere mixtures of an acid or a salt with a resin. Thus compositions containing mere mixtures of soluble acids or salts with or without resins or other organic materials are not resistant to leaching; in such mixtures the acid or the salt retains its physical and chemical characteristics such as acidity, liquid or crystalline state, melting point, etc. In the resin salt, on the contrary, the acid, or acid salt, is chemically combined, thereby losing its objectionable chemical and physical characteristics, but retaining its power to convert the resin into a carbonaceous mass when subjected to heat.

To prepare a fire-retardant resin salt, it is possible to condense the resin in the presence of the acid or acid salt; or the resin may be prepared in advance and then contacted with an aqueous solution of the acid.

In order to obtain a high degree of fire-retardance we have found that it is advantageous to apply the resin salt to combustible materials while the resin salt is still in a so-called water-soluble or incompletely polymerized state, and then cure the resin on or in the treated material. More particularly, highly combustible materials such as plywood, fibreboard and wallboard which require a high degree of fire protection are preferably coated with an aqueous solution of the resin salt and then subjected to polymerizing conditions, for example to heat to effect the curing of the resin salt in situ. When the resin salts of the preferred resins of class (4) with phosphoric acids are so used they form a continuous, strongly adhering film of excellent fire-retarding properties. When formed in this manner, the resinous coating on the combustible material is especially effective in its fire-retardant action, since it is not interfered with by the presence of other materials, such as film-forming bonding agents or fillers which are usually combustible organic materials or inert inorganic diluents and which therefore tend to decrease somewhat the effectiveness of the coating.

The degree of fire protection may be controlled by varying the thickness of the film. The thicker the film, or the greater the weight of coating per unit area, the better the protection.

In the water-soluble stage many resin salts tend to polymerize slowly on standing so that it is usually necessary to use them reasonably promptly after they have been prepared. This is perfectly possible in factory applications. For



example, in the manufacture of wallboard, solutions of resin salts may be made up in the morning for a day's production of wallboard. The solutions may be applied to the wallboard in a late stage of its manufacture.

However, it may not always be practical to use the above method of application. In many instances it is desirable to supply to the user a product which is stable on standing and which he may apply whenever convenient. For this purpose we polymerize the resin salt to a solid state, in which it is stable. We then disperse the solid resin salt in a finely-divided state in a liquid vehicle comprising a film-forming bonding agent, with or without a volatile thinner. Combustible materials can be coated with these compositions by spraying or painting or dipping or other suitable means. Upon evaporation of the thinner, a film is formed, which makes the solid resin salt dispersed in it adhere to the surface. Among film-forming agents we have found that drying oils, such as linseed oil, tung oil, dehydrated castor oil and the like are suitable although the dried oil film containing the resin salt reduces the latter's effectiveness not only because the oil film is itself somewhat inflammable, but because the film is sufficiently hard to interfere somewhat with the formation of the carbonaceous mass formed from the resin salt on exposure to flame temperatures. When drying oils are used, conventional paint thinners and driers may advantageously be used to complete the composition. More suitable film-formers than drying oils are film-forming resins, particularly alkyd resins. Among the alkyd resins we prefer the class of drying oil modified alkyds. These resins are not very combustible when well dried but they do interfere somewhat with the formation of the carbonaceous mass thereby reducing the effectiveness of the resin salt to some extent. Again conventional paint thinners may be used to complete the composition. Particularly suitable film-formers are cellulose ethers and cellulose esters in general, and especially methyl cellulose, ethyl cellulose, cellulose acetate and the like. These cellulose derivatives may be dissolved in an appropriate solvent (water, alcohol, etc.) and then the finely divided, solid, fully polymerized resin salt may be dispersed in this solution. The cellulose derivatives interfere less with the effectiveness of the resin salt than the drying oils or alkyds. While we have mentioned the above named film-forming agents as typical examples, it is clear that other film-forming agents may be used without departing from the scope of this invention.

Pigments and fillers may be added if desired.

The following specific examples illustrate how the invention may be carried out.

*Example I.*—This example illustrates how a preferred resin salt may be made and used according to this invention.

(a) 119 grams of guanidine carbonate and 126 grams of melamine were added to 322 grams of aqueous formaldehyde (37%). The ratio of the resin-forming ingredients was thus 4 mols of formaldehyde to 2 mols of combined guanidine and melamine and thus a 2:1 ratio between the formaldehyde and the cyanamide derivatives. The mixture was allowed to stand for 20 minutes. Then 42.5 cc. of concentrated phosphoric acid (85%  $H_3PO_4$ ) was added in small portions until the evolution of carbon dioxide stopped. The mixture was agitated continuously until an aqueous, slightly viscous dispersion was formed.

This dispersion gelled suddenly when heated on a steambath for about 15 minutes. The gel was cut into small pieces and dried at about 105° C. The dried gel was then washed with water, to remove any excess of unbound phosphoric acid, until the wash water was phosphate free. Thus was obtained a resin phosphate of excellent fire-retardant and potentially heat-insulating properties. The resin phosphate is remarkably water-insoluble, the phosphoric acid being chemically bound to the resin. Thus the solid product obtained is very different from a mere mixture of phosphoric acid, or one of its salts with a resin. It is substantially water-insoluble. It resists treatment by HCl,  $H_2SO_4$ , and HBr, showing that the resin phosphate is more stable than the sulfate, hydrochloride or hydrobromide. It is substantially irreversible in the sense that a substantial fraction of the phosphoric acid combined with the resin can no longer be removed by treatment with alkali. The product, when subjected for two minutes to a temperature of 750° C. in an electric furnace, expanded to a carbonaceous mass having a volume several times that of the original sample and this expanded mass remained substantially intact throughout the test.

(b) The slightly viscous aqueous dispersion obtained in (a) prior to gelling by heat was applied to one side of a wallboard by brushing. The wet board was heated at about 90° C. for three hours, whereby the water was evaporated and a uniform heat cured resin salt coat formed on the board. The coated board showed a greatly reduced inflammability on the coated side.

(c) 25 parts by weight of guanidine carbonate, 25 parts by weight of melamine and 62 parts by weight of aqueous formaldehyde (37%) were added to 60 parts of water. The ratio of the resin-forming ingredients was thus  $1\frac{2}{3}$  mols of formaldehyde to 1 mol of combined guanidine carbonate and melamine. To this mixture was added, very gradually and with thorough stirring, 42.5 parts by weight of phosphoric acid (85%).

In a typical factory test application, a fibreboard was sprayed with this resin salt solution. The treated wet fibreboard was then run through a hot air oven approximately 60 ft. long, heated to approximately 400° F., at a rate of 56 ft. of board per minute.

In another factory test application an untreated fibreboard was preheated by passage through a drying oven, was then sprayed with the resin salt solution and immediately thereafter subjected to the action of a metal-surfaced pressure roll, the surface temperature of which approximated 500° F.

In both cases there was obtained a fibreboard coated with a firmly adhering fire-retardant resin salt film of excellent appearance.

Plasticizers (for example p-toluene sulfonamide) and pigments may be added to the resin salt solution if desired.

(d) 200 lbs. titanium dioxide (Rutile), 400 lbs. of the fire-retardant resin salt of Example I(a) and 500 lbs. of alkyd resin (Falkyd No. A-3) were ground in a conventional paint mill and then dispersed in a mixture containing 118 lbs. of Solvesso No. 3 thinner, 3 lbs. of cobalt drier and 6 lbs. of lead drier. The resulting composition is stable on standing and may be shipped and stored if desired.

(e) 11.9 g. of guanidine carbonate and 12.6 g. of melamine were added to 32.4 cc. of aqueous formaldehyde (37%). The ratio of the resin-



forming ingredients was thus 2 mols of formaldehyde to 1 mol of combined guanidine carbonate and melamine. The solution was allowed to stand for two hours. Then about 1.5 cc. of concentrated phosphoric acid (85%  $\text{H}_3\text{PO}_4$ ) was added dropwise until the evolution of  $\text{CO}_2$  stopped, and the mixture was agitated continuously and with caution until it became thick. Then 8 cc. of concentrated phosphoric acid (85%  $\text{H}_3\text{PO}_4$ ) was added and heating continued until the mixture gelled. The gel was cut into small pieces, dried at about  $100^\circ\text{C}$ ., washed in running water for about 24 hours (the pH of the wash water was then about 6), again dried and ground in a ball mill. 6.3 g. of the resulting finely ground resin was then dispersed in a solution comprising 50 cc. of 95% ethyl alcohol and 1 g. of ethyl cellulose. The resulting composition is stable. It may be applied to paper, cardboard, fabrics and other combustible materials by immersion, roll coating, brushing, spraying or other suitable means. Upon evaporation of the alcohol and water from the coating, a fire-retardant material is obtained which is coated with the resin salt bound to it by the ethyl cellulose film. When the coated side is exposed to flame a fire-retardant and heat-insulating carbonaceous mass is formed.

(f) 12.5 grams of melamine, 12.5 grams of guanidine carbonate and 35 grams of aqueous formaldehyde (37%) were added to 400 cc. of water. The ratio of the resin-forming ingredients was thus slightly more than 2 mols of formaldehyde to 1 mol of combined melamine and guanidine. To this mixture 12.5 grams of concentrated phosphoric acid (85%  $\text{H}_3\text{PO}_4$ ) was added gradually. Samples of lightweight fabric were dipped into an impregnating bath containing the above liquid composition to which small quantities (for example less than 5% of the weight of the composition) of a plasticizer, such as for example paratoluene sulfonamide, or of urea, may be added. The impregnated fabric is squeezed and then placed in an oven at  $95^\circ\text{C}$ . for drying and curing for approximately 90 minutes. The treated fabric is substantially flame-proof.

(g) The aqueous resin dispersion of Example I(c) was used as an adhesive to bond (1) paper to paper, (2) paper to wood, and (3) wallpaper to insulation board. These materials were bonded by brushing the aqueous resin salt dispersion on both surfaces, pressing the surfaces together and curing by heat.

(h) To enhance the bonding properties a mixture of dry wheat paste and water containing 5 to 10% by weight of dry wheat paste, made to the consistency of a fluid paste (as conventionally used in hanging wallpaper) was mixed in equal parts with the aqueous resin dispersion of Example I(c) and used as in Example I(g). An improved bond was obtained particularly when wallpaper was bonded to the fibreboard.

A comparison of fire tests on the treated materials of Examples I(g) and I(h) with fire tests on controls in which the adhesive was the wheat paste of Example I(h) containing no resin salt showed a marked improvement in fire resistance of the materials of Examples I(g) and I(h) over the controls.

*Example II.*—60 grams of urea and 90 grams of guanidine carbonate were added to 300 cc. of aqueous formaldehyde (37%). The ratio of the resin-forming ingredients was thus slightly more than 2.1 mols of formaldehyde to 1 mol of com-

bined urea and guanidine carbonate. The solution was stirred without external heating for 35 minutes and an initial slight rise in temperature (to  $51^\circ\text{C}$ .) was noted. Then 22.7 cc. of concentrated sulfuric acid (sp. gr. 1.84) was added in small portions with continued stirring until the evolution of  $\text{CO}_2$  stopped. This solution may be used on combustible materials as described in Examples I(b) and I(c); or the solution may be heated for about 100 minutes on a steam bath until it becomes viscous and may then be dried at about  $120^\circ\text{C}$ . to constant weight. The resulting white, heat-cured solid resin sulfate may be ground to any desired mesh size, washed free of water-solubles, and may then be dispersed in a solvent containing a film-forming agent, as illustrated in Examples I(d) and I(e).

*Example III.*—25.2 g. of melamine and 23.8 g. of guanidine carbonate were added to 64.4 g. of aqueous formaldehyde (37%). The ratio of the resin-forming ingredients was thus 1.94 mols of formaldehyde to 1 mol of combined melamine and guanidine carbonate. The mixture was stirred and 9 cc. of concentrated sulfuric acid (sp. gr. 1.75) was added in small portions. At the end of the addition, no more  $\text{CO}_2$  was liberated and the pH had dropped to about 5. This composition may be applied to combustible materials as described in Examples I(b) and I(c). Or the mixture may then be heated on a steam bath and rapidly gelled at the end of five minutes. It may then be dried at  $110^\circ\text{C}$ . until its weight remains constant. This product possesses marked fire-retardance and potential heat-insulating properties.

*Example IV.*—18.1 g. of m-phenylenediamine dihydrochloride, 7.3 g. of concentrated HCl (36%) and 50 cc. of water were agitated at room temperature and 12 g. of aqueous formaldehyde were added. The temperature of the mixture rose to about  $45^\circ\text{C}$ . and a dark colored resin settled out almost immediately. This solid resin hydrochloride was separated from the solution and dried at  $105^\circ\text{C}$ . for 18 hours.

*Example V.*—18.1 g. of m-phenylenediamine dihydrochloride, 8.4 g. of dicyandiamide, 1.7 g. of concentrated HCl and 70 g. of water were heated on a steam bath for 24 hours to form a solution of biguanidylbenzene hydrochloride. This solution was cooled to  $50^\circ\text{C}$ . and a mixture of 36.2 g. of m-phenylenediamine dihydrochloride and 3.4 g. of concentrated HCl was added. This mixture was allowed to cool to  $30^\circ\text{C}$ . and 52.7 g. of aqueous formaldehyde (37%) were then added slowly. Almost instantly a gel was formed and the temperature rose to about  $80^\circ\text{C}$ . The dark solid resin hydrochloride was dried at  $103^\circ\text{C}$ . for 18 hours. This resin hydrochloride showed very marked fire-retardance and resistance to combustion in the furnace test. A porous carbonaceous heat-insulating mass forms on exposure to  $750^\circ\text{C}$ . in the furnace. The mass is reasonably resistant to combustion.

The products of Examples IV and V are primarily suitable for use in conjunction with film-forming agents as described in Examples I(d) and I(e).

*Example VI.*—9.4 g. of phenol, 14.6 g. of triethylene tetramine and 24.3 g. of aqueous formaldehyde (37%) were carefully mixed with external water cooling; 25 g. of aqueous formaldehyde were then added and the mixture was heated on the steam bath until it gelled. The gel was dried at  $125^\circ\text{C}$ . This basic resin is inflammable. When it is reacted with about 3 milli-



equivalents of phosphoric acid per g. of basic resin it forms a resin salt of greatly reduced inflammability which is, in conjunction with a film-forming agent and a solvent, valuable as a fire-retardant and potential heat-insulator.

*Example VII.*—12 g. of triethylene tetramine, 25 g.  $H_3PO_4$  (85%), 35 g. aqueous formaldehyde (37%) and 125 g. of acetone were refluxed for 1 hour. The light acetone layer was separated from the heavier viscous resinous layer formed. The viscous polymer may be applied to combustible materials, before or after curing by heat to form a fire-retardant coat.

It should be noted that the solid resin salt of this invention may also be used to form molded or otherwise fabricated, substantially non-inflammable articles, or may be used as a dust to protect combustible materials against fire.

We claim:

1. An article of manufacture comprising a base member having as a fire retardant protective surface, an adherent continuous dry coating comprising a reaction product of a basic anion-exchange resinous co-condensation product of a weakly basic derivative of cyanamide selected from the group consisting of urea, thiourea, dicyandiamide and melamine, a strongly basic derivative of cyanamide selected from the group consisting of guanidine and substituted guanidine and formaldehyde with the formaldehyde being in a proportion of at least  $1\frac{2}{3}$  mols to 1 mol of the combined content of said cyanamide derivatives, and at least 2 milliequivalents per gram of said resinous co-condensation product of a strong non-oxidizing inorganic acid having a dissociation constant of at least  $10^{-3}$ , said coating, when heated to an elevated temperature, being converted into a heat-insulating carbonaceous mass.
2. An article of manufacture as defined in claim 1, wherein the weakly basic derivative of cyanamide is urea and the strongly basic derivative of cyanamide is guanidine.
3. An article of manufacture as claimed in claim 1, wherein the weakly basic derivative of cyanamide is urea and wherein the strongly basic derivative of cyanamide is guanylurea.
4. An article of manufacture as claimed in claim 1, wherein the weakly basic derivative of cyanamide is urea and the strongly basic derivative of cyanamide is guanylurea and wherein the inorganic acid is phosphoric acid.
5. An article of manufacture as claimed in claim 1, wherein the resinous co-condensation product comprises melamine, guanylurea and formaldehyde and wherein the inorganic acid is phosphoric acid.
6. An article of manufacture comprising a base member having as a fire-retardant protective surface, an adherent dry film of an organic film-forming bonding agent in continuous phase having dispersed therethrough a finely divided reaction product of a basic anion-exchange resinous co-condensation product of a weakly basic derivative of cyanamide selected from the group consisting of urea, thiourea, dicyandiamide and melamine, a strongly basic derivative of cyanamide selected from the group consisting of guanidine and substituted guanidine and formaldehyde with the formaldehyde being in a proportion of at least  $1\frac{2}{3}$  mols of formaldehyde to 1 mol of combined content of said cyanamide derivatives, and at least two milliequivalents per gram of said resinous co-condensation product of a strong non-oxidizing inorganic acid having a

dissociation constant of at least  $10^{-3}$ , said coating, when heated to an elevated temperature, being converted into a heat-insulating carbonaceous mass.

7. A liquid film-forming composition capable of imparting fire retardant properties to combustible materials when applied thereto and dried thereon, comprising a room temperature liquid mixture of incompletely polymerized basic-anion-exchange-co-condensation resin-forming ingredients consisting essentially of a weakly basic derivative of cyanamide selected from the group consisting of urea, thiourea, dicyandiamide and melamine, a strongly basic derivative of cyanamide selected from the group consisting of guanidine and substituted guanidine and an aqueous formaldehyde solution with the formaldehyde being in a proportion of at least about  $1\frac{2}{3}$  mols of formaldehyde to 1 mol of combined content of said cyanamide derivatives, and at least 2 milliequivalents per gram solids of said resin-forming ingredients of a strong non-oxidizing inorganic acid having a dissociation constant of at least  $10^{-3}$ , said composition in the form of a dried film being converted by heat at elevated temperature into a heat-insulating carbonaceous mass.

8. A liquid composition as claimed in claim 7, wherein the resin-forming ingredients comprise urea, guanylurea and formaldehyde.

9. A liquid composition as claimed in claim 7, having, as an additional ingredient, a carbohydrate and wherein the inorganic acid is phosphoric acid.

10. A liquid composition as claimed in claim 7 having, as an additional ingredient, an adhesive.

11. A liquid paint capable of imparting fire retardant properties to combustible materials upon application of said paint thereto, comprising a liquid organic film-forming vehicle having suspended therein in dispersed phase a finely divided reaction product of a basic anion-exchange resinous co-condensation product of a weakly basic derivative of cyanamide selected from the group consisting of urea, thiourea, dicyandiamide and melamine, a strongly basic derivative of cyanamide selected from the group consisting of guanidine and substituted guanidine and formaldehyde with the formaldehyde being in a proportion of at least about  $1\frac{2}{3}$  mols of formaldehyde to 1 mol of combined content of said cyanamide derivatives, and at least 2 milliequivalents per gram of said co-condensation product of a strong non-oxidizing inorganic acid having a dissociation constant of at least  $10^{-3}$ , said paint in the form of a dried film being converted by heat at elevated temperature into a heat-insulating carbonaceous mass.

12. A paint as claimed in claim 11 having, as additional ingredients, a carbohydrate and a paint pigment.

13. A paint capable of imparting fire retardant properties to combustible materials, comprising an intimate mixture of a cellulosic bonding agent and a finely divided reaction product of a basic-anion-exchange resinous co-condensation product of urea, guanylurea and formaldehyde with the formaldehyde being in a proportion of at least about  $1\frac{2}{3}$  mols of formaldehyde to 1 mol of combined content of said urea and guanylurea, and at least 2 milliequivalents per gram of said co-condensation product of phosphoric acid, said paint in the form of a dried film being converted by heat at elevated temperature into a heat-insulating carbonaceous mass.



14. A paint as claimed in claim 13, wherein the cellulosic bonding agent is ethyl cellulose.

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### Certificate of Correction

Patent No. 2,628,946

February 17, 1953

WALTER JUDA ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 1, for "2,36,086" read 2,362,086; column 7, line 35, for that portion of the formula reading "NH<sub>2</sub>" read NH<sub>2</sub>; line 38, for "dicyandiamide" read *dicyandiamidine*; column 9, line 17, for "paintaing" read *painting*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 2nd day of June, A. D. 1953.

[SEAL]

THOMAS F. MURPHY,

Assistant Commissioner of Patents.