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PARTIALLY DEHALOGENATED REACTIVE
DERIVATIVES OF THE HALOGENATION
PRODUCTS OF THE MONO HETERO
ATOMIC FIVE MEMBERED RINGS

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This invention relates to the partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings as well as to the methods for pre-
paring said products.

In a more specific aspect, the invention relates
to the partially dehalogenated reactive deriva-
tives of the substantially fully saturated halo-
genation addition products of the aldehydes of
furan and its homologues as well as to the
methods for preparing said products.

In a preferred aspect, the invention relates to
the partially dechlorinated reactive derivatives of
the aldehydes of furan and its homologues as well
as to the methods for preparing said products.

An object of the present invention is to provide
partially dehalogenated reactive derivatives of
the substantially fully saturated halogenation ad-
dition products of the aldehydes of the mono
hetero atomic five membered rings which can ad-
vantageously be used in lieu of the aforesaid satu-
rated halogenation products.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are less violently reactive
than the saturated halogenated aldehydes from
which they are derived.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are more reactive than the
original saturated halogenated aldehydes.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are possessed of a more
fluid character than the original saturated halo-
genated aldehydes.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are of a more viscous
character than the original saturated halogenated
aldehydes.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five

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membered rings which are grindably hard and
may be ground or pulverized.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are particularly suitable
for use as curing agents.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are particularly suitable
for use as vulcanizing agents for products of a
rubbery nature.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are particularly suitable
for use as hardening agents for resinous products.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are particularly useful as
curing agents for use in solution for purposes of
hardening or vulcanizing resinous or rubbery
products.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are suitable for use as cur-
ing agents for hydroxy (OH) group containing
polymers to convert the same to a substantially
infusible, thermo rigid, or vulcanized rubbery
state, the said polymer containing, on a weight
basis, a hydroxy (OH) group content of not less
than $\frac{1}{10}$ of one per cent nor more than 56.8 per
cent.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are suitable for use as
curing agents for partially saponified polyvinyl
esters, polyvinyl alcohols, and the polyvinyl ace-
tals.

A further object is to provide partially dehalo-
genated reactive derivatives of the substantially
fully saturated halogenation addition products of
the aldehydes of the mono hetero atomic five
membered rings which are useful as chemical in-
termediates.

A further object is to provide partially dehalogenated reactive derivatives of the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings which are useful in the manufacture of dyestuffs, pharmaceuticals, photographic chemicals, tanning agents, solvents, plasticizers, resins, synthetic rubber compounding ingredients, etc., etc.

The partially dehalogenated reactive derivatives of the substantially fully saturated halogenation addition products of the mono hetero atomic five membered rings are all produced by the method comprising reacting one or more of the aforesaid saturated halogenated aldehydes under conditions calculated to achieve a partial dehalogenation.

The partially dehalogenated reactive derivatives referred to in the present invention permit of ready distinction and characterization in that, (1) they are all derived from the saturated halogenation products of the mono hetero atomic five membered rings, (2) they all contain more than 25 per cent and less than 100 per cent of the halide atoms contained in the saturated halogenated aldehydes from which they are derived, and (3) they all enter into reaction with substances such as tetraethylene pentamine upon heating, not infrequently with violence.

In its simplest aspect the products of the present invention are produced either by simply subjecting the substantially fully saturated halogenation addition products of the mono hetero atomic five membered rings to the action of heat or to the action of any one of innumerable reagents. Representative of suitable agents for reaction with the aforementioned saturated halogenated products are the following: water; ammonia and all manner of ammonia derivatives; alkali metals, oxides and hydroxides; alkaline earth metals, oxides and hydroxides; heavy metals, as well as their oxides and hydroxides in the active state; carbonates, sulphides, sulphites, borates, the salts of weak inorganic acids, as well as the salts of virtually all organic acids; and organic compounds of all sorts, virtually without qualification. The objective of any reaction is to achieve the partial dehalogenation.

In reacting the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings the only requisite is that the reaction conditions as regards pressure, temperature, time, etc., as well as the chemical co-reagent, if any, be such that the dehalogenation shall not be carried beyond the point where more than 75 per cent of the halogenated aldehyde's original halide content is removed. When more than three-quarters of the original halogen content is removed in the process of dehalogenation, then the resultant reaction products may be characterized as falling outside of the scope of reactivity with which the herein described products are possessed. The dehalogenated products which retain less than 25 per cent of the original halogenated aldehyde's halogen content are either but slightly reactive or non-reactive. These products are extremely useful for a wide variety of purposes, but they do not take the place of the "reactive" products of the present invention.

The substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings as well as the methods of preparing the same are fully described

in copending application, Serial No. 464,524, filed November 4, 1942.

Briefly and generically described, the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings are produced by the method which comprises the steps of diluting a mole of one or more of the said aldehydes with at least a mole of solvent, and then rapidly introducing halogen in the proportion of substantially four atoms of halogen per molecule of the said aldehyde while maintaining the temperature below the point of spontaneous decomposition. A more specific procedure is shown by the method of chlorinating furfural, which comprises the steps of diluting a mole of said aldehyde with at least a mole of solvent and then rapidly introducing chlorine in the proportion of substantially four atoms of chlorine per molecule of the said aldehyde, while maintaining the temperature below the point of spontaneous decomposition.

Of the known aldehydes of the mono hetero atomic five membered rings furfural is by far the most abundant and, indeed, because of its agricultural origin, may be said to be inexhaustible. For this reason the present inventors, in the majority of the ensuing illustrative examples, list as the specific progenitor the halogenation product of furfural. It should be clearly understood, however, that the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings other than furfural are usable.

Chlorine is by far the most abundant, most available, and most widely distributed halogen element in the earth's crust. For this reason, in most of the ensuing examples, the present inventors have, for purposes of illustration, listed the chlorinated aldehydes in preference to the other halogenated aldehydes. It is to be distinctly understood, however, that the halogenation products other than those of chlorine, that is fluorine, bromine, and iodine, are also usable in the present invention.

As has already been indicated the partially deavailable mono hetero atomic five membered ring aldehyde is furfural, while chlorine is by far the most practical halogen. For these reasons, then, the saturated chlorination product of furfural is shown as the specific reactant in many of the following illustrative examples in which the quantities are stated in parts by weight.

As has already been indicated, the partially dehalogenated reactive derivatives of the present invention can be prepared by subjecting to suitable heat treatment, the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings. A more specific embodiment consists in subjecting the substantially fully saturated chlorination addition product of furfural to the action of heat either per se or in the presence of a substantially inert diluent. (It is to be understood that under appropriate conditions of reaction virtually all manner of so-called "substantially inert diluents" can be made to react, e. g., in the presence of substances as anhydrous aluminum chloride, etc.)

Example I

Chlorinated furfural (chlorine content 59%), 47.6 parts, is heated to a temperature of approximately 370° F. under a pressure of from 100 to 300 mm. of Hg. The rate of heating may be so regulated that the processing is completed in ap-

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proximately two to three hours, and the final weight of residuum should be between 41 and 42 parts. The above product is decidedly more fluid than the original chlorinated furfural and is possessed of a chlorine content of 55.07 per cent.

Example II

Chlorinated furfural, 47.6 parts, is subjected to the action of heat under a pressure of from 100 to 300 mm. of Hg at a maximum temperature of 400° F. The reaction may be completed in approximately four hours so that one ends up with between 35 and 36 parts of partially dehalogenated reactive material.

Example III

Chlorinated furfural, 47.6 parts, is subjected to the action of heat under a pressure of from 100 to 300 mm. of Hg at a maximum temperature of 400° F. The reaction may be completed in approximately four hours so that one ends up with between 28.5 and 29.5 parts of partially dehalogenated reactive material.

Example IV

Chlorinated furfural, 47.6 parts, is subjected to the action of heat under a pressure of from 100 to 300 mm. of Hg, and finally under a pressure of less than 20 mm. of Hg. The maximum temperature may be in the neighborhood of 390° F. and the operation may be completed in five and one-half hours so that one ends up with a residuum of 23.3 to 24.3 parts.

It will be noted that in each of the above four examples chlorinated furfural was subjected to a heat treatment which was varied in severity. It is also possible to carry out the heat treatment under conditions of super-atmospheric pressure or at atmospheric pressure or at pressures lower than those indicated, and for each condition, it is possible to procure partially dehalogenated reactive derivatives.

Example V

A mixture comprising 47.6 parts of chlorinated furfural and 47.6 parts of xylene is refluxed for a period of five hours. The mixture is then partially distilled, first under a pressure of from 100 to 300 mm. of Hg, and then under a pressure of less than 20 mm. of Hg. The temperature may advantageously be kept at 325° F. and the heat is maintained until the rate of distillation appreciably slows up and the weight of residuum falls within the range of approximately 35 to 38 parts. This dehalogenated reactive derivative contained 53.5 per cent of chlorine, possessed an acid number of 126, a saponification number of 173, a mean molecular weight of approximately 450, and a specific gravity of 1.619.

Example VI

A mixture comprising 47.6 parts of chlorinated furfural and 23.8 parts of xylene is refluxed for approximately three hours, and then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg, while maintaining a temperature of approximately 325° F. The processing is continued until the rate of distillation drops down and the weight of residuum falls within the range of from 34 to 35 parts. This product analyzed 55.72 per cent of chlorine.

Example VII

A mixture comprising 47.6 parts of chlorinated furfural and 11.9 parts of xylene is refluxed for

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approximately three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg. Approximately 36 to 37 parts of residuum are procured.

Example VIII

A mixture comprising 47.6 parts of chlorinated furfural and 47.6 parts of xylene is refluxed for a period of approximately five hours and is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg. The heating is continued until a residuum weighing between 20 and 21 parts and containing approximately 51.25 per cent of chlorine is obtained.

The four examples immediately preceding illustrate the partial dechlorination of chlorinated furfural in the presence of a "substantially inert" solvent. Countless other solvents or diluents may be employed including aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, etc. There is evidence that in almost every case the so-called substantially inert solvent or diluent is slightly attacked. It has also been found that if appropriate catalysts such as anhydrous aluminum chloride be added to the reaction, very profound reactions may occur between the solvent and the chlorinated furfural.

Example IX

A mixture comprising 52.5 parts of chlorinated furfural and 96.0 parts of methanol is refluxed for a period of about ten hours when a loss in weight of approximately 18.0 parts will occur. The loss in weight is almost exclusively due to evolved methyl chloride. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg, when a yield of approximately 45.5 parts of a partially dehalogenated reactive derivative results. This product analyzed carbon 36.67 per cent, hydrogen 3.99 per cent, chlorine 31.22 per cent, oxygen 28.1 per cent, acid number 21.05, saponification number 744, specific gravity 1.414 and methoxy group content 21.45 per cent.

Example X

A mixture comprising 47.56 parts of chlorinated furfural and 32.08 parts of methanol is refluxed until an initial loss in weight of approximately 5.1 parts occurs. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield approximately 42.6 parts of a partially dehalogenated reactive derivative containing 43.65 per cent of chlorine and 15.25 per cent of methoxy.

Example XI

A mixture comprising 47.56 parts of chlorinated furfural and 16.04 parts of methanol is refluxed until an initial loss in weight of approximately 5.1 parts occurs. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield approximately 42.4 parts of a partially dehalogenated reactive derivative containing 42.0 per cent of chlorine and 14.13 per cent of methoxy.

Example XII

A mixture comprising 47.56 parts of chlorinated furfural and 8.02 parts of methanol is re-

fluxed until an initial loss in weight of approximately 5.1 parts occurs. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield approximately 41.8 parts of a partially dehalogenated reactive derivative containing 43.0 per cent of chlorine and 12.06 per cent of methoxy.

Example XIII

A mixture comprising 47.56 parts of chlorinated furfural and 8.02 parts of methanol without any preliminary reflux is immediately subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield approximately 44.85 parts of a partially dehalogenated reactive derivative containing 48.5 per cent of chlorine and 8.76 per cent of methoxy.

Example XIV

A mixture comprising 47.56 parts of chlorinated furfural and 16.04 parts of methanol without any preliminary reflux is immediately subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield approximately 42.0 parts of a partially dehalogenated reactive derivative containing 44.3 per cent of chlorine and 12.12 per cent of methoxy.

Example XV

A mixture comprising 47.56 parts of chlorinated furfural, 64.08 parts of methanol, and 1.8 parts of water is refluxed until an initial loss in weight of approximately 5.1 parts occurs. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 41.6 parts of a partially dehalogenated reactive derivative containing 37.07 per cent of chlorine and 16.01 per cent of methoxy.

Example XVI

A mixture comprising 47.56 parts of chlorinated furfural, 32.08 parts of methanol, and 3.6 parts of water is refluxed until an initial loss in weight of approximately 5.1 parts occurs. The mixture is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 38.55 parts of a partially dehalogenated reactive derivative containing 38.0 per cent of chlorine and 11.8 per cent of methoxy.

Example XVII

A mixture comprising 47.6 parts of chlorinated furfural, 16.04 parts of methanol, and 1.8 parts of water without any preliminary reflux is immediately subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 41.6 parts of a partially dehalogenated reactive derivative containing 44.07 per cent of chlorine and 9.05 per cent of methoxy.

Example XVIII

Calcium carbonate, 5.0 parts, is slowly added to a solution comprising 47.6 parts of chlorinated furfural dissolved in 70.0 parts of methanol. The mixture is then heated and kept hot for a short period of time and is then concentrated under a pressure of from 100 to 300 mm. of Hg to a weight of approximately 70.5 parts. The further processing is optional, but the following gives good

results: To the concentrate add 60.0 parts of benzene, and 32.0 parts of water. Shake, separate the layers, dry the benzene layer, filter and, if desired, clarify with decolorizing carbon. The benzene solution is then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield approximately 40.9 parts of an amber colored partially dehalogenated reactive derivative containing 40.47 per cent of chlorine and 16.44 per cent of methoxy.

Example XIX

Twenty parts of calcium carbonate (powdered marble flour) is slowly added to a solution comprising 47.6 parts of chlorinated furfural dissolved in 70.0 parts of methanol. After heating for a short period with continued agitation the mixture is subjected to slow vacuum concentration under a pressure of from 100 to 300 mm. of Hg. The concentrate may, from this point on, be processed as follows: Add benzene and water, agitate, let stratify, decant the benzene layer, dry the latter and, if desired, clarify with decolorizing carbon and then distill off the benzene, preferably under reduced pressure at a temperature below 250° F. Approximately 37.0 parts of a light amber colored partially dehalogenated reactive derivative containing 39.25 per cent of chlorine and 20.1 per cent of methoxy is obtained.

Example XX

Zinc dust, 3.27 parts, was slowly added to a mixture consisting of 47.6 parts of chlorinated furfural and 32.08 parts of methanol. The mixture was cooled down to prevent excessive loss through volatilization. The mixture was subjected to partial distillation under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 31.1 parts of a partially dehalogenated reactive derivative which contained 24.5 per cent of chlorine and 4.28 per cent of methoxy. The above weight and percentage data includes the zinc chloride synthetically formed.

Example XXI

Zinc dust, 0.327 part, was slowly added to a mixture consisting of 47.6 parts of chlorinated furfural and 16.0 parts of methanol. The mixture was subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 29.7 parts of a partially dechlorinated reactive derivative containing approximately 25.8 per cent of chlorine and 5.89 per cent of methoxy. Zinc dust and zinc salts, e. g., zinc chloride function as catalysts resulting in a vigorous reaction accompanied by a copious evolution of methyl chloride.

Example XXII

Zinc chloride, 0.68 part, was added to a mixture consisting of 47.6 parts of chlorinated furfural and 16.04 parts of methanol. The mixture was subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 30.8 parts of a partially dehalogenated reactive derivative which contained 30.4 per cent of chlorine and 7.86 per cent of methoxy. The product of this reaction was a grindably hard mass.

Example XXIII

Zinc chloride, 0.68 part, was added to a mixture consisting of 47.6 parts of chlorinated furfural and

32.08 parts of methanol. The mixture was refluxed for four hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield a grindably hard solid product weighing 24.8 parts. This partially dechlorinated reactive derivative contained 22.4 per cent of chlorine and 3.87 per cent of methoxy. It is interesting to note that when catalysts such as powdered zinc or zinc salts are employed, the resultant compounds are possessed of a much lower ether or methoxy content than in the absence of such a catalyst.

Example XXIV

A solution comprising 4.1 parts of anhydrous sodium acetate dissolved in 32.08 parts of methanol was added to 47.6 parts of chlorinated furfural. The mixture was then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 45.7 parts of a residuum which contained some NaCl. Sixty parts of benzene and 36.0 parts of water were added to the above residuum and after agitation, the stratified layers were separated. The benzene layer was then dried, decolorized, and filtered and the benzene was then distilled off under reduced pressure to yield 39.0 parts of a partially dehalogenated reactive derivative which contained 44.6 per cent of chlorine and 8.66 per cent of methoxy besides some acetal groups.

Example XXV

A solution comprising 11.2 parts of potassium hydroxide dissolved in 60.0 parts of methanol was slowly added to a mixture consisting of 47.6 parts of chlorinated furfural dissolved in 20.0 parts of methanol. The mixture was subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg. Sixty parts of benzene and 36.0 parts of water were then added to the residuum and the resultant mixture after shaking, was permitted to stratify and the benzene layer was removed, dried, decolorized, and finally freed from the benzene by vacuum concentration. Approximately 36.0 parts of a partially dechlorinated reactive derivative were procured.

Example XXVI

A mixture comprising 15.0 parts of chlorinated furfural and 39.5 parts of anhydrous ethanol was refluxed for a period of approximately thirty-three hours. A large quantity of ethyl chloride was evolved. The mixture was then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 11.6 parts of a partially dehalogenated reactive ethoxy containing derivative which analyzed carbon 45.15 per cent, hydrogen 5.04 per cent, chlorine 20.35 per cent, oxygen 28.45 per cent and ethoxy 26.55 per cent.

Example XXVII

Calcium carbonate, 10.0 parts, was slowly introduced into a mixture consisting of 47.6 parts of chlorinated furfural and 100.15 parts of anhydrous ethanol. The mixture was concentrated under a pressure of between 100 and 300 mm. of Hg so as to yield 83.0 parts of residuum. Then 36.0 parts of water and 60.0 parts of benzene were added, the mixture agitated, the layers permitted to stratify, and the organic layer removed. The

latter was then dried, decolorized, filtered and then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 35.5 parts of a partially dehalogenated reactive ethoxy containing derivative which analyzed carbon 40.0 per cent, hydrogen 4.29 per cent, chlorine 32.0 per cent and ethoxy 15.2 per cent.

Example XXVIII

Chlorinated furfural, 14.3 parts, was dissolved in 49.0 parts of normal butanol and the resultant mixture was then subjected to slow distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 12.4 parts of a reactive derivative which analyzed 51.0 per cent carbon, 7.07 per cent hydrogen, 16.1 per cent chlorine, and 25.85 per cent oxygen.

Example XXIX

A mixture comprising 15.0 parts of chlorinated furfural and 63.25 parts of normal butyl alcohol was refluxed for four hours and then subjected to distillation at atmospheric pressure. Fresh quantities of butanol were introduced to replace that which distilled off. The mixture was then subjected to an additional refluxing for four hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 12.82 parts of a partially dechlorinated reactive derivative which analyzed 57.3 per cent carbon, 7.25 per cent hydrogen, 9.32 per cent chlorine, and 26.14 per cent oxygen.

Example XXX

A mixture comprising 10.9 parts of chlorinated furfural and 46.0 parts of iso-butanol was subjected, first to slow fractional distillation at atmospheric pressure and then to partial distillation first under a pressure of 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 11.16 parts of a reactive derivative which analyzed carbon 55.45 per cent, hydrogen 7.62 per cent and chlorine 13.91 per cent.

Example XXXI

A mixture comprising 47.6 parts of chlorinated furfural and 37.06 parts of iso-butanol without any preliminary refluxing was immediately subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 45.66 parts of a reactive derivative which contained 37.3 per cent of chlorine.

Example XXXII

A mixture comprising 14.07 parts of chlorinated furfural and 59.25 parts of a secondary butyl alcohol was subjected first to slow fractional distillation at atmospheric pressure and then to direct partial distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 11.11 parts of a reactive derivative which analyzed 52.5 per cent carbon, 6.1 per cent hydrogen, and 17.2 per cent chlorine.

Example XXXIII

A mixture comprising 4.76 parts of chlorinated furfural and 5.92 parts of tertiary butyl alcohol was subjected to slow fractional distillation at atmospheric pressure. Very considerable quantities of gas were evolved. The mixture was then

subjected to direct distillation at atmospheric pressure and finally under a pressure of less than 20 mm. of Hg to obtain 9.09 parts of derivative. Tertiary alcohols of all sorts are more or less completely decomposed by the saturated halogenation products of the aldehydes of the mono hetero atomic five membered rings.

Example XXXIV

A mixture comprising 13.0 parts of chlorinated furfural and 65.5 parts of secondary amyl alcohol is refluxed for a period of about twelve hours, and then subjected to fractional distillation at atmospheric pressure, then to direct distillation under reduced pressure, first under a moderate vacuum and finally under a pressure of less than 20 mm. of Hg. A reactive derivative, 10.07 parts, is procured which analyzed carbon 52.0 per cent, hydrogen 5.69 per cent and chlorine 7.07 per cent.

Example XXXV

A mixture comprising 47.6 parts of chlorinated furfural and 27.6 parts of secondary amyl alcohol without any preliminary refluxing is immediately subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 41.27 parts of a partially dehalogenated reactive derivative which contained 40.85 per cent of chlorine.

Example XXXVI

A mixture comprising 47.6 parts of chlorinated furfural and 27.6 parts of secondary amyl alcohol is directly subjected to distillation under a pressure of less than 20 mm. of Hg to yield 39.83 parts of a reactive derivative containing 41.7 per cent of chlorine.

Example XXXVII

A mixture comprising 12.0 parts of chlorinated furfural and 35.0 parts of tetrahydro furfuryl alcohol is subjected to slow distillation at atmospheric pressure and then to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield approximately 21.0 parts of a slightly rubbery reactive residuum which contained about 11.32 per cent of chlorine. If the heating be continued, a more rubbery product is procured and if the heating be still further continued, a substantially infusible hard rubbery material results.

Example XXXVIII

A mixture comprising 10.5 parts of chlorinated furfural and 65.0 parts of benzyl alcohol was heated and then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg. The somewhat rubbery partially dehalogenated reactive residuum contained 15.92 per cent of chlorine.

Example XXXIX

A mixture comprising 47.6 parts of chlorinated furfural and 38.03 parts of the mono methyl ether of ethylene glycol was directly subjected to partial distillation under a pressure of less than 20 mm. of Hg to yield 43.52 parts of a partially dehalogenated reactive derivative which contained 37.22 per cent of chlorine and had an alkoxy content equivalent to 7.48 per cent calculated as methoxy.

Example XXXX

A mixture comprising 47.6 parts of chlorinated

furfural and 18.02 parts of the mono ethyl ether of ethylene glycol was directly subjected to partial distillation under a pressure of less than 20 mm. of Hg to yield 45.64 parts of a reactive derivative whose alkoxy content was 10.24 per cent, calculated as ethoxy.

Example XXXXI

A mixture comprising 47.6 parts of chlorinated furfural and 58.08 parts of butyl acetate was first refluxed four hours and then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 44.2 parts of a reactive derivative which contained 47.8 per cent of chlorine.

Example XXXXII

A mixture comprising 47.6 parts of chlorinated furfural and 31.02 parts of ethylene glycol was directly subjected to partial distillation under a pressure of less than 20 mm. of Hg to yield 44.1 parts of a partially dehalogenated derivative which contained 31.33 per cent of chlorine.

Example XXXXIII

A mixture comprising 47.6 parts of chlorinated furfural and 40.0 parts of ethylene chlorhydrin is directly subjected to partial distillation under a pressure of less than 20 mm. of Hg to yield 44.4 parts of a reactive derivative which contained 50.05 per cent of chlorine.

Example XXXXIV

A mixture comprising 47.6 parts of chlorinated furfural and 29.0 parts of acetone (dimethyl ketone) was refluxed four hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 41.3 parts of a reactive derivative containing 51.2 per cent of chlorine.

Example XXXXV

A mixture comprising 47.6 parts of chlorinated furfural and 36.05 parts of ethyl methyl ketone was refluxed for two hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 41.0 parts of a partially dechlorinated reactive derivative containing 51.9 per cent of chlorine.

Example XXXXVI

A mixture comprising 47.6 parts of chlorinated furfural and 56.06 parts of di-isobutylene was first refluxed for a period of four hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield 39.7 parts of a reactive derivative containing 38.6 per cent of chlorine.

Example XXXXVII

A mixture comprising 47.6 parts of chlorinated furfural, 23.8 parts of xylene, and 16.04 parts of methanol was refluxed for three hours and then subjected to partial distillation under a pressure of less than 20 mm. of Hg to yield 26.36 parts of a reactive derivative containing 46.2 per cent of chlorine and 4.19 per cent of methoxy.

Example XXXXVIII

A mixture comprising 47.6 parts of chlorinated furfural, 32.0 parts of butanol, and 0.68 part of anhydrous zinc chloride was refluxed for four

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hours and then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield 23.89 parts of a grindably hard reactive derivative containing 14.91 per cent of chlorine.

Example XXXIX

A mixture comprising 24.0 parts of chlorinated furfural, 36.0 parts of mono methyl ether of ethylene glycol and 2.0 parts of distilled water was refluxed for eight hours and then subjected to distillation, first at atmospheric pressure, then under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg, ending up with a kettle jacket temperature of approximately 425° F. and continuing the reaction until the product acquired a rubbery character. A yield of approximately 11.0 parts of a black rubbery product was procured. The material analyzed chlorine 5.3 per cent, hydrogen 5.6 per cent and carbon 52.2 per cent. This particular derivative was still perspective reactive. Had the heating and distillation been stopped earlier a more fluid and more reactive product would have been procured and vice versa, had the heating and vacuum distillation been continued beyond the point to which it was carried, then substantially infusible, rubbery, and hard products are obtained which test substantially non-reactive. When chlorinated furfural or its equivalent is reacted with the mono methyl or mono ethyl ether of ethylene glycol a very large quantity of alkyl halide is generated.

Example L

A mixture comprising 2.38 parts of chlorinated furfural and 3.6 parts of butyl aldehyde is refluxed for four hours and then subjected to partial distillation first at atmospheric pressure and then under a pressure of less than 20 mm. of Hg until at a temperature of 300° F. nothing further distills off. A yield of 3.36 parts is procured which analyzed 70.7 per cent of carbon, 8.38 per cent of hydrogen, and 7.56 per cent of chlorine.

Example LI

A mixture comprising 2.38 parts of chlorinated furfural, 4.64 parts of the methyl ester of alpha-methoxy isobutyric acid was refluxed for three hours and then subjected to partial distillation under a pressure of less than 20 mm. of Hg at a temperature of 340° F. to yield 1.26 parts of a reactive product.

Example LII

Anhydrous aluminum chloride, 2.67 parts, is cautiously added to a mixture comprising 4.2 parts of chlorinated furfural and 4.7 parts of benzene. The mixture was then refluxed upon a water bath for about two hours and then 20.0 parts of water and 8.0 parts of benzene were added along with a little hydrochloric acid and the mixture was refluxed for thirty minutes. The mixture was then permitted to cool, the layers separated, and the benzene solution was decolorized, filtered, and then concentrated by evaporation at a temperature of 212° F. at a pressure of less than 20 mm. of Hg. A more or less reactive hard product weighing 5.67 parts was procured.

Example LIII

Anhydrous aluminum chloride, 2.67 parts was slowly added to a mixture comprising 4.2 parts of chlorinated furfural and 12.4 parts of benzene.

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The mixture was kept cool for a period of one hour and the temperature was then permitted to come up to that of the room and finally it was subjected to refluxing for about one-half hour, then cooled somewhat. Water, benzene and a little hydrochloric acid were added and the mixture subjected to a short reflux, cooled, the layers separated (which latter operation was expedited through the addition of further quantities of hydrochloric acid) filtered, and evaporated off the solvents under a pressure of less than 20 mm. of Hg so that 4.87 parts of a derivative were procured which analyzed carbon 72.1 per cent, hydrogen 4.81 per cent and chlorine 13.77 per cent.

Example LIV

Anhydrous aluminum chloride, 2.67 parts, was added to a mixture consisting of 4.2 parts of chlorinated furfural and 20.23 parts of di-isobutylene. After the aluminum chloride had been added the mixture was permitted to cool somewhat and 1.0 part of hydrochloric acid along with 20.0 parts of water were added. The mixture was refluxed thirty minutes. After cooling the layers were separated. The organic layer was filtered and the benzene and excess di-isobutylene, etc., were distilled off, yielding 7.61 parts as the derivative.

Example LV

A mixture comprising 4.5 parts of chlorinated furfural and 3.1 parts of α -terpineol was heated upon a water bath for one hour. The temperature was then raised to 300° F. under a pressure of between 100 and 300 mm. of Hg and then to 350° F. under the same pressure until a grindably hard product weighing 4.29 parts was procured.

Example LVI

Live steam was passed into a mixture comprising 8.0 parts of chlorinated furfural and 15.0 parts of xylene. The steam was passed in for a period of approximately six and one-half hours and the mixture was then subjected to partial distillation, first under a pressure of 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg ending up with a yield of 3.75 parts of derivative.

Example LVII

A mixture comprising 4.0 parts of chlorinated furfural, 12.0 parts of diethylene glycol and 3.53 parts of water was refluxed for a period of several hours and then subjected to partial distillation, first under a pressure of 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg, ending up with a residuum weighing 2.59 parts.

Example LVIII

A mixture comprising 4.0 parts of chlorinated furfural, 12.0 parts of the diethyl ether of ethylene glycol and 1.77 parts of water was refluxed and the evolved gases were collected, then switched to partial distillation, first under a pressure of 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg ending up with a reactive chlorine containing residuum of 1.32 parts. The material was black in color, grindably hard, and had a rather high melting point.

Example LIX

A mixture comprising 4.0 parts of chlorinated furfural and 8.0 parts of aqueous (40%) formal-

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dehyde was refluxed for eight hours and then after separating the layers, the organic layer was distilled under a pressure of from 100 to 300 mm. of Hg to yield 2.56 parts of a moderately hard, solid material possessed of a fair reactivity.

Example LX

A mixture comprising 12.0 parts of chlorinated furfural and 24.0 parts of aqueous solution containing 40% formaldehyde was refluxed for seven hours and then distilled, first at atmospheric pressure and then under a pressure of between 100 and 300 mm. of Hg. The heating was continued until, at a temperature of approximately 300° F., a grindably hard resinous product weighing 8.70 parts was procured. The material had a capillary tube melting point of approximately 121° F. and analyzed 12.14 per cent chlorine. The product reacted readily with various reagents.

Example LXI

A mixture comprising 16.0 parts of chlorinated furfural and 32.0 parts of aqueous formaldehyde solution, which latter containing 40% of formaldehyde, was refluxed for fifteen hours while the evolved gases were collected. The pressure was then reduced between 100 and 300 mm. of Hg and the mixture was subjected to partial distillation, ending up with a temperature of approximately 300° and a grindably hard resinous mass weighing 11.81 parts which analyzed 10.63 per cent chlorine.

Example LXII

A mixture comprising 4.0 parts of chlorinated furfural and 4.0 parts of cotton seed oil was heated to 300° F. for thirty minutes, then at 325° F. for two hours, and finally at 350° F. for about two hours. Considerable quantities of gaseous product (HCl) were evolved. If the mixture be heated for a further period of time then the product passes over into a rubbery composition. Material of this sort by being subjected to temperature in excess of 350° F. for a period of two or more hours can be converted into a material suitable for the manufacture of friction elements and brake blocks.

Example LXIII

A mixture comprising 8.0 parts of chlorinated furfural and 24.0 parts of water was refluxed for a period of one hour. The material was in two layers, one in an aqueous phase and the other in an organic phase. The mixture was then subjected to partial distillation under a pressure of 100 to 300 mm. of Hg yielding 3.68 parts of derivative analyzing 26.45 per cent chlorine.

Example LXIV

A mixture comprising 6.0 parts of chlorinated furfural and 8.0 parts of raw linseed oil was heated to a temperature of 350° F. and held there until it gelled. A gelatinous product weighing 12.07 parts was procured. During the reaction considerable quantities of HCl were evolved.

Example LXV

A mixture comprising 6.0 parts of chlorinated furfural and 8.0 parts of palm oil fatty acid was heated to 350° F. This temperature was maintained until the product gelled (one hour). Considerable quantities of hydrogen chloride were evolved and the yield of derivative was 11.67 parts. In a somewhat analogous manner all types of vegetable and animal oils, fats, waxes and

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their fatty acids may be reacted including rosin, turpentine, and all manner of related products.

Example LXVI

A solution consisting of 4.76 parts of chlorinated furfural dissolved in 7.0 parts of methanol was added to a solution comprising 6.56 parts of anhydrous sodium acetate dissolved in 35.0 parts of methanol. The mixture was then refluxed for one hour and let cool. The product was suction-filtered, the filtrate being washed with an additional quantity of methanol. The filtrate was then subjected to partial evaporation, first at atmospheric pressure and then under a pressure of from 100 to 300 mm. of Hg. A residuum of 9.0 parts resulted. This latter was then extracted with anhydrous ethyl acetate, filtered and reconcentrated so as to evaporate off the ethyl acetate. The residuum which comprised the main reaction product weighed 4.0 parts and had a chlorine content of approximately 10 per cent.

Example LXVII

Anhydrous aluminum chloride, 2.67 parts, was added to a mixture comprising 4.2 parts of chlorinated furfural and 19.39 parts of mono chloro benzene. Approximately one and one-half hours was utilized in introducing the aluminum chloride at the end of which time the mixture was kept cool for an additional thirty minutes, and thereafter, it was refluxed for a period of one hour. The mixture was then cooled to 140° F. and 1.0 part of concentrated hydrochloric acid and 20.0 parts of water were added. The material was refluxed for thirty minutes, the layers separated, the organic layer filtered and the latter then subjected to partial distillation under a pressure of from 100 to 300 mm. of Hg until at an end temperature of 400° F. nothing further distilled over. A yield of 8.33 parts of a highly viscous material resulted.

Example LXVIII

A mixture comprising 9.52 parts of chlorinated furfural and 1.84 parts of glycerine is heated to 212° F. for a period of two hours, then at 275° F. for a period of one hour, then at 300° F. for a period of one hour, and finally at 300° F. for a period of one hour under a pressure of from 100 to 300 mm. of Hg. Approximately 7.6 parts of a partially dechlorinated reactive derivative resulted. The quantity of glycerine employed may be varied between rather wide limits and a time-temperature schedule other than that indicated may be used. Utilizing 9.52 parts of chlorinated furfural and the indicated time-temperature schedule, the following yields of reactive products result, when one utilizes the following respective quantities of glycerine: Parts glycerine—1.23, 1.84, 2.0, 2.5, 3.0, 3.68, 4.0, 4.5, 5.52; the yield of reactive product equals 7.26, 7.6, 7.7, 7.84, 8.39, 9.10, 9.25, 9.55 and 10.57 parts respectively. Reactive products such as the above are capable of curing or setting up such products as sugar, dextrose, corn sugar, formal sugars, caramel, acetone-formaldehyde reaction products, etc.

Example LXIX

A mixture comprising 9.52 parts of chlorinated furfural and 3.68 parts of caramel (prepared from sucrose) was heated first at 212° F. and then at a higher temperature of 250° F. The ultimate material was possessed of a high melting point

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and with slightly more heating, passes over into an infusible product.

Example LXX

A mixture comprising 9.52 parts of chlorinated furfural and 3.68 parts of sorbitol was heated first at 212° F., then at 250° F., then at 275° F., and finally for two hours at 300° F. A yield of 8.10 parts of reactive product resulted.

Example LXXI

Butadiene is passed into 4.214 parts of chlorinated furfural dissolved in 5.786 parts of carbon tetrachloride. The mixture is kept under conditions of reflux and the gas is passed in for a period of eight or more hours. The bulk of the carbon tetrachloride is then distilled off under atmospheric pressure and finally the temperature is stepped up to 212° F. with a reduction in pressure to between 100 to 300 mm. of Hg. Approximately 4.41 parts of a reactive product result.

Example LXXII

Five and sixty-five hundredths parts of a solution containing 2.38 parts of chlorinated furfural dissolved in carbon tetrachloride is added to 13.6 parts of a solution comprising 1.36 parts of natural rubber dissolved in benzene. The mixture is stirred and refluxed for a period of one hour and is then concentrated until the residuum weighs approximately 8.5 parts. The mixture is then further refluxed for an hour and is then subjected to partial distillation at atmospheric pressure when 3.43 parts of a semi-stiff rubbery mass is procured. This latter is then extracted with methanol so as to remove unreacted chlorinated furfural, etc. We end up with 2.25 parts of a product of moderate reactivity which contains 18.45 per cent of chlorine.

Example LXXIII

A mixture comprising 47.6 parts of chlorinated furfural and 1.8 parts of water without any preliminary refluxing is directly subjected to partial distillation under a pressure of from 100 to 300 mm. of Hg until approximately 41.6 parts of a reactive derivative containing about 53 per cent of chlorine is obtained as the residuum. It was noted that when the indicated quantity of water was used, the reaction or dehalogenation proceeded at approximately twice the rate at which reaction occurs under similar conditions but in the absence of water.

Example LXXIV

A solution comprising 12.14 parts of 28 per cent aqueous ammonia dissolved in 12.14 parts of methanol is slowly added to a solution of 47.6 parts of chlorinated furfural dissolved in 47.6 parts of methanol. The mixture is concentrated under a pressure of from 100 to 300 mm. of Hg and then water and benzene are added to aid in washing out water-soluble material such as ammonium chloride. The benzene layer is separated, filtered and may, if desired, be dried and clarified with a decolorizing carbon. The benzene layer is then subjected to partial distillation to remove benzene, preferably under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg while maintaining the temperature preferably not above 250° F. The resultant reactive derivative, besides containing chlorine, contains nitrogen. Considerable leeway is permissible as regards the amount of ammonia that may be utilized in these reactions. It is also possible to use more or less diluent or to

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use a diluent other than the indicated methanol. Finally, it should be emphasized that instead of ammonia one may utilize materials such as ammonium carbonate, ammonium acetate, ammonium sulphide, ammonium iodide, as well as any of the simpler organic amines such as the mono methyl, di methyl, or tri methyl amine or the corresponding ethyl, propyl, isopropyl, butyl, etc. amines. In this manner it is possible to procure any number of reactive derivatives which contain the element, nitrogen, as an integral part of the derivative.

Example LXXV

A solution consisting of 9.3 parts of aniline dissolved in an equal weight of methanol is slowly added to a solution comprising 47.6 parts of chlorinated furfural dissolved in 47.6 parts of methanol. The mixture is concentrated under a pressure of from 100 to 300 mm. of Hg and the resultant concentrate is then washed with a mixture of benzene in water. The benzene layer is then separated, dried, clarified, and subjected to partial distillation so as to remove the benzene and other ready volatiles. The resultant dark colored product which may range in consistency anywhere from a material resembling very heavy molasses to a soft solid contains besides chlorine the element, nitrogen. Considerable leeway is permissible as regards either the quantity of aniline employed or the quantity or type of diluent used. In lieu of aniline one may employ any one of a host of other aromatic or heterocyclic amines, e. g., ortho toluidine, para toluidine, xylenes, amines of naphthols, amines of anthraquinones, amines of phenanthracenes, etc. Polyamino compounds may similarly be utilized.

Example LXXVI

A solution containing 9.4 parts of phenol dissolved in an equal weight of methanol is slowly added to a mixture comprising 47.6 parts of chlorinated furfural dissolved in 47.6 parts of methanol and the whole is slowly heated and may, if desired, be refluxed for a period of one hour or so or else is directly subjected to partial distillation so as to procure a concentrate amounting to approximately 75 parts by weight. The resultant concentrate may then be washed with a mixture of water and benzene, the benzene layer separated, dried, clarified, and subjected to partial distillation under a reduced pressure so as to remove the ready volatiles. The resultant black colored material may range in consistency from a very viscous fluid to a soft solid. If desired, the water washing step may be dispensed with and the product may be directly subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg. Considerable leeway is permissible as regards the quantity of phenol employed as well as in the matter of the quantity and type of diluent and the time-temperature schedule. Further, in lieu of phenol other phenolic materials may be utilized, e. g., cresols, xylenols, naphthols, as well as various substituted phenols, e. g., tertiary amyl phenol, para chlor phenol, and para nitro phenol.

Example LXXVII

A mixture comprising 10.9 parts of para amino phenol dissolved in an equal quantity of methanol is slowly added to a mixture comprising 47.6 parts of chlorinated furfural dissolved in an equal weight of methanol. The mixture is immedi-

ately subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield a black colored reactive residuum. If desired, the initial mixture may first be concentrated to a weight of about 75 parts and the latter then subjected to water washing and extraction with benzene, etc. As in the previous two examples, here too considerable leeway is permissible as regards the quantity of amino phenol employed, the quantity and type of diluent and in the matter of the time-temperature schedule. To the best of our knowledge any of the amino phenols may be utilized in this reaction. Amino phenols substituted with hydrocarbon, halide, or nitro groups are also usable.

Example LXXVIII

A solution comprising 7.8 parts of sodium mono sulphide (anhydrous basis) dissolved in a mixture of aqueous methanol is added to a solution comprising 47.6 parts of chlorinated furfural dissolved in an equal weight of methanol. The mixture is refluxed for a period of about one hour and is then concentrated to a weight of about 75 parts. Water and benzene are added to the concentrate and the organic layer is then separated, dried, clarified, and subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg. The resultant reactive chlorine containing compound also contains the element, sulphur. Appreciable quantities of H₂S are evolved.

Example LXXIX

A mixture comprising 47.6 parts of chlorinated furfural, 47.6 parts of benzene and 16.7 parts of mercapto benzothiazole is subjected to direct partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg. The resultant reactive chlorine containing derivative is found to contain the element, sulphur. Considerable leeway is permissible as regards the quantity of the organic sulphur compound, the type and quantity of diluent, as well as in the matter of the time-temperature schedule. In lieu of the above indicated mercapto benzothiazole one may employ any one of thousands of other organic compounds containing sulphur or its analogues, e. g., benzo thiazole disulphide, zinc dimethyl dithio carbamate, zinc diethyl dithio carbamate, zinc dibutyl dithio carbamate, tetramethyl thiuram disulphide, tetraethyl thiuram disulphide, selenium diethyl dithio carbamate, 2-mercapto-thiazoline, thiourea, urea and the cyclo hexamine derivative of mercapto benzo thiazole, 2,2'-dithio-bis-benzothiazole, thio carbanilide, salts of pentamethylene-dithio carbamate, piperidinium pentamethylene-dithio carbamate, diphenyl thiourea, dipentamethylene thiuram tetra sulphide, tetramethyl thiuram monosulphide, aldehyde amine thiazole, etc.

Example LXXX

A mixture comprising 16.6 parts of potassium iodide dissolved in 100.0 parts of methanol is added to a solution of 47.6 parts of chlorinated furfural dissolved in an equal weight of methanol. The mixture is refluxed for a period of three hours and is then concentrated to a weight of approximately 75 parts. Water and benzene are added. The benzene layer is separated, dried, clarified and finally subjected to partial distillation to remove the ready volatiles. The resultant

chlorine containing reactive derivative also contains the element, iodine. Considerable leeway is permissible as regards the reaction conditions and in lieu of potassium iodide one may employ such materials as ammonium iodide, caesium iodide, rubidium iodide, sodium iodide, lithium iodide, barium iodide, strontium iodide, calcium iodide, magnesium iodide, etc. More or less elemental iodine is liberated in these reactions.

Example LXXXI

A mixture comprising 11.7 parts of di-ethyl-amino ethanol dissolved in an equal weight of methanol is slowly added to a solution of 47.6 parts of chlorinated furfural dissolved in an equal weight of methanol. The mixture is refluxed for a period of three hours and is then subjected to partial distillation, first under a pressure of between 100 and 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg. An optional alternative is, after the refluxing operation, to concentrate the mixture to a weight of about 75 parts and then to add water and benzene, mix thoroughly, let stratify, separate the benzene layer, dry and clarify the same and then subject to partial distillation under reduced pressure for the purpose of removing the benzene and other ready volatiles. Amino alcohols, hydroxy acids, amino acids, lactones, lactides, lactanes, etc., may be used in lieu of the above di-ethylamino ethanol.

Example LXXXII

A mixture comprising 49.0 parts of chlorinated methyl furfural and 64.0 parts of methanol is refluxed for three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield a partially dehalogenated chlorine containing reactive derivative.

Example LXXXIII

A mixture comprising 47.7 parts of chlorinated α -pyrrole aldehyde and 64.0 parts of methanol is refluxed for a period of three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield a partially dehalogenated chlorine and nitrogen containing derivative.

Example LXXXIV

A mixture comprising 49.2 parts of chlorinated thiophen aldehyde and 64.0 parts of methanol is refluxed for three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield a partially dehalogenated reactive chlorine and sulphur containing derivative.

Example LXXXV

A mixture comprising 83.2 parts of brominated furfural and 64.0 parts of methanol is refluxed for a period of three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and then under a pressure of less than 20 mm. of Hg to yield a partially dehalogenated reactive bromine containing derivative.

Example LXXXVI

A mixture comprising 120.8 parts of iodinated furfural and 64.0 parts of methanol is refluxed for three hours and is then subjected to partial distillation, first under a pressure of from 100

to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield a partially dehalogenated reactive iodine containing derivative. It is noted that when working with the iodine compounds appreciable amounts of elemental iodine come into being as is evidenced by the gaseous or vaporous phases possessing a violet colored hue and oftentimes iodine crystals are formed either on the sides of the reaction kettle in the condenser or in the receiver.

Example LXXXVII

A mixture comprising 34.4 parts of the reaction product of fluorine and furfural (prepared at low temperatures in carbon ware with the fluorine electrolytically produced from hydrogen fluoride and immediately passed into the furfural which is diluted with di-chloro-di-fluoro methane sufficiently cooled to prevent the diluent from distilling out during the halogenation) dissolved in 64.0 parts of methanol is refluxed for a period of three hours and then subjected to partial distillation, first under a pressure of from 100 to 300 mm. of Hg and finally under a pressure of less than 20 mm. of Hg to yield a reactive fluorine containing derivative. It appears that fluorine compounds, which incidentally, are exceedingly difficult, costly, and hazardous to prepare, are less reactive than the chlorine compound, apparently because a large percentage of the fluorine atoms are more firmly attached than in the instance of the chlorine atom.

The above examples are purely illustrative and by no means exhaust the list of possible reactants or reaction conditions. When chlorinated furfural is used as the base reactant one may utilize as the inorganic reactant such substances as water, ammonia, hydroxylamine, sulphides, iodides, bromides, as well as the alkali and alkaline earth metal salts or compounds of any of the non-metallic elements including sulphur, selenium, tellurium, phosphorus, nitrogen, etc.

The number of known organic compounds is many times as extensive as the known inorganic compounds. Organic compounds are, therefore, of particular interest as reactants for the halogenated aldehydes of the mono hetero atomic five membered rings for the purpose of producing reactive derivatives. Under appropriate conditions of reaction one may utilize virtually any one of the known organic compounds with the possible exception of compounds such as carbon dioxide, carbon monoxide, carbon tetrachloride, etc., and even these compounds under appropriate conditions of catalysis and in the presence of another reactant can be utilized in the preparation of reactive derivatives out of the halogenation products of the aldehydes of the mono hetero atomic five membered rings.

It is essential that when the substantially fully saturated halogenation addition products of the aldehydes of the mono hetero atomic five membered rings are reacted the conditions be such that at least one-quarter of the original halide atoms remain in the reaction product otherwise the same will be insufficiently reactive to permit its classification with the herein referred to "reactive" products. The more powerful dehalogenating agents such as the alkali metals and alkaline earth metals as well as materials such as finely divided iron powder, magnesium powder, zinc powder, etc. are generally speaking too energetic and violent in their action to permit their direct use in the absence of a diluent. The oxides and hydroxides of the alkali metals and alkaline earth

metals likewise may be considered as being too energetic to permit their use in the absence of a diluent. Most organic bases, particularly the polyamines, react very violently, sometimes with explosive force with the halogenated aldehydes and in order to achieve an effective control and a uniformity of product, it is necessary to utilize a suitable diluent. As has already been pointed out, alcohols, e. g., methanol, react with the halogenated aldehydes to form ethers and in very many instances such ether formation is not at all undesirable, but to the contrary, is often an advantage. It is, therefore, feasible and convenient to utilize a material such as methanol as the diluent and in this way the said diluent functions at the same time as a reactant. Thus, when sodium hydroxide is brought into contact with chlorinated furfural an exceedingly energetic, erratic, non-uniform and uncontrollable reaction occurs. If, however, the chlorinated furfural be dissolved in methanol and the sodium hydroxide be likewise dissolved in either methanol, aqueous methanol or water, and the same then cautiously added to the methanol solution of the chlorinated furfural, a comparatively smooth reaction occurs. The resultant reaction product will, to be sure, contain some methoxy groups but this in most instances is permissible. In the instance of alcohol insoluble organic products, benzene is often a suitable working medium.

Oftentimes it is desirable to perform a series of operations upon the halogenated aldehydes. Thus, one may first react chlorinated furfural with methanol after the manner of some of the above examples and then the resultant reaction product may be further reacted with a reagent of an altogether different nature, e. g., a methanol solution of potassium iodide, sodium sulphide, aniline, ammonia, phenol, urea, etc.

Although the partially dehalogenated reactive derivatives of the present invention are generally procured and isolated as the residuum, it is also possible in many instances to procure the same in the form of a distillate. This is best accomplished by subjecting the material to distillation under very high vacuum or by a molecular still. Chlorinated furfural, upon heat treatment at elevated temperatures under a very high vacuum, largely distills over into a somewhat dehalogenated reactive derivative. The products resulting from the reaction between chlorinated furfural and large quantities of methanol or the reaction products procured by reacting chlorinated furfural with methanol in the presence of calcium carbonate, caustic soda, etc., or finally the products resulting from reaction between chlorinated furfural and a salt such as sodium acetate in the presence of methanol (methoxylated-acetylated derivatives) lend themselves more readily to high vacuum distillation than the majority of the other derivatives.

Referring to organic co-reactants, chlorinated furfural, or in its broader aspects the halogenation products of the aldehydes of the mono hetero atomic five membered rings, can be made to react with the aliphatic, carbocyclic and heterocyclic classes of organic compounds. The presence of specific functional groups, such as alcoholic hydroxy groups, phenolic hydroxy groups, carbonyl groups, amino groups, etc. facilitate the reaction. As a consequence, chlorinated furfural will combine more readily with alcohols, ketones, esters, amines, acids, nitro-derivatives, etc., than with the parent substances.

Chlorinated furfural can be converted to reac-

tive derivatives by reacting the same with all manner of aliphatic hydrocarbons whether saturated or unsaturated and non-aromatic carbocyclic compounds. It is often necessary to use a catalyst such as an aluminum halide to procure reaction. In many instances appropriate compounds of zinc, iron, antimony, arsenic, molybdenum, vanadium, etc. exert a catalytic effect upon the reactions. Under appropriate conditions of thermal and chemical environment, chlorinated furfural can be converted to reactive derivatives by reacting the same with alkanes, alkenes, alkadienes, alkatrienes, alkynes, alkadiynes, alkapolynes, cyclanes, spiranes, bicyclanes, polycyclanes, cyclenes, bicyclenes, polycyclenes, etc. Chlorinated furfural can react more readily with compounds containing unsaturated linkages than with the fully saturated compounds. Hydrocarbons that are of a type that readily undergo auto-reaction, e. g., isomerization or polymerization, generally react either faster or more thoroughly than do the less reactive, more stable compounds.

Chlorinated furfural can be converted to reactive derivatives by reacting the same with all manner of aromatic or carbocyclic compounds. Here too, the presence of a suitable catalyst such as an aluminum halide is desirable. Thus, the chlorinated furfural can be made to react with the alkyl benzenes, alkenyl benzenes, alkadienyl benzenes, alkatrienyl benzenes, alkynyl benzenes, as well as with the condensed aromatics such as the indanes, indenenes, fluorenes, naphthylenes, anthracenes, phenanthrenes, naphthacenes, aromatic-cyclane hydrocarbons, aromatic-cyclene hydrocarbons, aromatic-cyclodiene hydrocarbons, etc. All manner of compounds belonging to the so-called class of terpenes can be made to react quite readily with chlorinated furfural to yield partially dechlorinated reactive derivatives.

The reactive derivatives that are procurable via the reaction of chlorinated furfural with aliphatic or carbocyclic hydrocarbons are of a most diverse nature. As a rule, complicated mixtures of complex products come into being. In instances the reaction products are of a stable, fusible character and in other instances they are non-fusible. It should be noted that hydrogen chloride is almost invariably engendered in these reactions. In the instance of some of the more complex unsaturated hydrocarbons, a part of the hydrogen chloride may be absorbed into the complex by way of an addition reaction. The reaction products with but few exceptions are dark in color, a deep amber, brownish-black and black—in many instances, of course, via processes of distillation or decoloration in one manner or another, many of the products can be lightened.

Chlorinated furfural can be converted to reactive derivatives by reacting the same with all manner of heterocyclic compounds. Specifically we here mention:

Mono-heteroatomic three membered rings (e. g., ethylene oxide, ethylene sulfide and ethylene imine).

Di-heteroatomic three membered rings (hydrazide and azomethylene group, and diazomethane).

Mono-heteroatomic four membered rings (trimethylene oxide and trimethylene imine).

Di-heteroatomic four membered rings (betaines, thetines, methylene urea, and methylene thiourea).

Mono-heteroatomic five membered rings (furans, thiophenes, pyrroles, coumarones, thio-

naphthenes, indoles, diphenylene oxide group, diphenylene sulfide group, dibenzo pyrroles, etc.).

Poly-heteroatomic five membered rings (pyrazoles, indazoles, isoxazoles, indoxazenes, glyoxalines, benzoglyoxalines, oxazoles, benzoxazoles, thiazoles, benzothiazoles, osotriazoles, pyrro-diazoles, furazans, azaximes, oxydiazoles, furo-diazoles, thio-diazoles, thio-triazoles, and tetra azoles).

Mono-heteroatomic six membered rings, e. g., six membered rings with an oxygen member (pyrones, benzo derivatives, coumarins, flavone, luteolin, xanthene, fluoranes, xanthone, etc.); six membered rings containing a nitrogen member (pyridine group, e. g., pyridines, halogen pyridines, sulphonic acids, nitropyridines, pyridones, thiopyridines, pyridyl alcohols, pyridyl ketones, pyridine carboxylic acids, oxypyridine carboxylic acids, hydropyridines, piperideines, piperidines, quinolines, condensed quinolines, isoquinolines, phenanthridines, naphthyridines, quindolines, acridines, anthrapyridines); poly-heteroatomic six membered rings (oxazines, thiazines, diazines, triazines, tetrazines); poly-heteroatomic six membered rings which contain both oxygen and sulphur members as well as the vegetable alkaloids.

The reactive products that result from the reaction between chlorinated furfural and heterocyclic compounds (often in the presence of a catalyst) are of the most diverse nature imaginable. Generally speaking, however, these reaction products, prior to purification, are dark in color and all contain more or less chlorine. Some of the compounds are fusible, others are non-fusible, and almost invariably they are of a higher complex nature. These reaction products like those of the other hydrocarbons serve as useful intermediaries for the production of other compounds and are of interest from the standpoint of resins, rubbers, pharmaceuticals, dyestuffs, insecticides, etc., etc.

The introduction of a non-hydrocarbon reactive functional group into a molecule of a hydrocarbon facilitates the potential reactivity of the resultant substituted compound with chlorinated furfural. The greater the number of such functional groups present in the molecule of the reactant, the more readily it reacts. Generally speaking, chlorinated furfural will react with many hydrocarbons which contain non-hydrocarbon substituting groups, often quite readily upon heating in the absence of a catalyst. Chlorinated furfural will react in this wise with all manner of non-hydrocarbon substituted organic compounds to yield partially dehalogenated reactive derivatives. It is to be distinctly understood, however, that the reaction conditions as regards the proportions and the time-temperature schedule must be deliberately calculated so as not to result in an elimination of more than six of the original halide atoms, as otherwise the resultant product will be substantially "non-reactive." Specific mention may be made of the following representative classes of compounds (although in the case of chlorinated furfural, as herein specifically referred to, it is to be distinctly understood that more or less analogous reactions are engaged in by all of the other halogenation products of the aldehydes of the mono hetero atomic five membered rings):

Chlorinated furfural can be converted over into reactive derivatives by reaction with the halogenated derivatives of the hydrocarbons, irrespective of whether they be saturated or un-

saturated aliphatic carbocyclic, heterocyclic or mixed.

Chlorinated furfural can be converted over into reactive derivative by reaction with all the oxidation derivatives of the aliphatic hydrocarbons including the monohydric alcohols, unsaturated alcohols, olefine alcohols, acetylene alcohols, diolefine alcohols, simple and mixed ethers and esters of mineral acids, sulphur derivatives of alcohol radicals, selenium, tellurium, nitrogen and phosphorous derivatives of the alcohol radicals, alkyl derivatives of arsenic, antimony, boron, silicon, germanium and tin, metallo organic compounds, all manner of aldehydes whether aliphatic, carbocyclic or heterocyclic, ketones including their halogenation substitution products, peroxides (ethers and esters), sulphur derivatives, nitrogen derivatives, as well as the olefines and diolefine aldehydes and ketones.

Chlorinated furfural can be converted over into reactive derivatives by reaction with the mono and poly basic carboxylic acids of the saturated and unsaturated type whether aliphatic, carbocyclic or heterocyclic, also their anhydrides and nitriles.

Chlorinated furfural can be quite readily converted over into reactive derivatives by reaction with the dihydric alcohols and their oxidation products, e. g., glycols, (ethers and esters), thio compounds, nitrogen derivatives, aldehyde alcohols, ketone alcohols, ketols, di-aldehydes, ketone aldehydes, di-ketones, carboxylic acids, hydroxy olefine acids, aldehyde acids, ketonic carboxylic acids (whether saturated or unsaturated), as well as their innumerable haloid, sulphur and nitrogen derivatives.

Chlorinated furfural can easily be converted into reactive derivatives by reaction with the trihydric alcohols, di-hydroxy ketones, hydroxy di-aldehydes, hydroxy aldehyde ketones, hydroxy ketones, di-aldehyde ketones, aldehyde di-ketones, tri-ketones, di-hydroxy monocarboxylic acids, monoaminocarboxylic acids, monoaminothio-carboxylic dimonoaminocarboxylic acids, dihydroxy olefine monocarboxylic acids as well as their esters, etc.

Chlorinated furfural can be converted over into reactive derivatives by reaction with penta-, hexa-, and poly-hydric alcohols and their oxidation products, e. g., pentitols, aldopentoses, hexitols, heptahydric alcohols, oxyhydric alcohols, monohydric alcohols, polyhydroxy aldehydes and ketones, aldehydes, ketohexoses, aldoheptoses, aldo-octoses, aldononses, hexaketones, as well as the various carboxylic acids, ethers and esters that are derivable from the above polyhydric alcohols. Included in this category are all the various sugars, starches, etc.

Chlorinated furfural reacts with all manner of proteins and albuminous substances.

Partially dehalogenated reactive derivatives can be procured by reacting chlorinated furfural with substantially any of the derivatives of the carbocyclic compounds, e. g., the derivatives derivable from the tri, tetra, penta, hexa, hepta, octo and mono-carbocyclic compounds. Thus, it can react with the non-hydrocarbon substitution products of the mono-nuclear aromatic substances, e. g., the halogen derivatives, nitrogen derivatives including the nitro and nitroso derivatives, hydroxylamines, nitrosohydroxylamines, analines, diamines, nitrosamines, nitramines, diazo compounds, diazo-amido-compounds, diazo-oxy-amido-compounds, ozoxy-compounds, azo-compounds and hydrazine compounds. Chlorinated

furfural can be made to react with the aromatic compounds of phosphorous, arsenic, antimony, bismuth, boron, silicon, tin as well as with the metal derivatives such as magnesium biphenyl, aryl-magnesium haloids, mercury diphenyls, etc. Chlorinated furfural can react with all the sulfonic acids and all their derivatives, phenols, quinones, aromatic alcohols, and their oxidation products, e. g., the phenyl-paraffin alcohols, aromatic mono-aldehydes, aromatic mono-ketones, aromatic mono-carboxylic acids, and aromatic poly-carboxylic acids as well as their innumerable derivatives including the esters, acids, haloids, acid anhydrides, acid peroxides, thio-acids and bi-thio-acids, acid amides, acid hydrazides, acetyl-azides, nitriles, amido-haloids, imido chlorides, phenyl-hydrazine-imido-chlorides, imido-ethers of the aromatic acids, thiamides of the aromatic acids, imido-thio-ethers and the amidines of the aromatic acids, di-oxy-tetra-azotic acids, hydrazidins, nitrazones, nitrotriazones, phenyl-azoxines, formazyl derivatives, hydroxamic acids, ethers and esters, haloids of the benzo-hydroxamic acid, benzo-nitrolic acid, benzo-nitrolisic acid, nitrile oxides, amidoximes, hydrazidoximes, hydraxamoximes, ethyl ortho benzoic esters, benzo-trichlorides and trifluorides, ortho benzoic acid piperidides, the various other substituted aromatic acids. Chlorinated furfural can be made to react with the oxy-phenyl-paraffin alcohols and their innumerable alcohols, aromatic oxy-mono-aldehydes, phenyl-ketones, phenyl-carboxylic acids, polyhydric aromatic alcohols in which one or more hydroxyl groups are present in each side chain as well as their oxidation products, aromatic substances with unsaturated side chains, e. g., olefine benzenes, acetylene benzenes, diolefine benzenes, olefine-acetylene-benzenes, olefine-phenols, acetyl-anisols, phenyl-olefine alcohols, and their oxidation products, oxy-phenyl-olefine-carboxylic acids, as well as the oxidation products of aromatic poly-alcohols with unsaturated side chains, e. g., phenylene-oxy-olefine-carboxylic acids, phenyl-diolefine-a-keto-carboxylic acids, cyano-cinnamic acid, phenylene-oxy-olefine-dicarboxylic acids.

Reactive derivatives may be procured by reacting chlorinated furfural with all manner of hydro-aromatic substances with one or more nuclei including all their derivatives and substitution products, e. g., the halogen, nitro and amino substitution products of the cyclohexanes, hexa-hydrobenzenes, naphthenes, cyclo-hexanes, tetrahydro-benzenes, naphthylenes, di-hydro-benzenes, cyclo-hexa-dienes, ring alcohols of the hydro-aromatic hydrocarbons, e. g., cyclo-hexanol, quinite, queroite, inosite, phenose, the ring alcohols of the tetra-hydro-benzenes, extra cyclo-hydro-aromatic alcohols as well as their derivatives, ring amines of the hydro-aromatic hydrocarbons, e. g., amido-cyclo-hexanes, extra cyclo-hydro-aromatic amines, ring ketones of the hydro aromatic hydrocarbons, hydro-aromatic aldehydes, e. g., cyclo citral, extra cyclo-hydro-aromatic ketones, hydro-aromatic carboxylic acids, e. g., hydro-aromatic mono-carboxylic acids, hexa-hydro-oxy-benzoic acids, quinic acid, shikimit acid, succino-succinic acid.

Partially dehalogenated reactive derivatives can be procured by reacting halogenated aldehydes with all manner of terpenes, e. g., the olefinic terpene group (myrcene, coimene, isotrene, as well as their various haloid substitution products, etc.), the olefinic terpene alcohols, olefinic terpene aldehydes, olefinic terpene acids, mono-

cyclic terpenes, e. g., limonene, terpinolene, terpinene, phellandrene, alcohols of the monocyclic terpenes, e. g., menthane alcohols, secondary menthols, tertiary menthols, mono, di, and poly-acid alcohols, bases and ring ketones of the monocyclic terpenes. Chlorinated furfural quite readily reacts with the dicyclic terpenes as well as the sesqui terpenes and poly-terpenes, e. g., thujene, sabinane, carone, eucarvone, pinene, turpentine oil, terebinic acid, myrtenol, pinol, camphene group comprising camphene bornylene, fenchene, borneol, iso-borneol, camphor, fenchone, candinene, santalol, caoutchouc.

Reactive derivatives may be procured by reacting chlorinated furfural with all manner of aromatic hydrocarbons containing several nuclei, e. g., phenyl benzols, and the polyphenyl fatty hydrocarbons and all their derivatives and substitution products including the phenyl-benzoles, benzo-benzoles, triphenyl methanes, phenyl derivatives of the triphenyl carbinols, phenyl-bis-di-phenyl-methanes, tetra - phenyl - methanes, homologous di- and polyphenyl paraffins and the condensed nuclei type and all their derivatives.

We have already pointed out that the presence of a non-hydrocarbon functionally reactive group in a hydrocarbon molecule further enhances the reactability and the reaction possibilities with the halogenation products of the aldehydes of the mono hetero-atomic five membered rings. Specifically it may be stated by way of example that a hydrocarbon compound containing one or more of the following structural groupings, complexes, or radicals will in general react either more readily, more thoroughly, or in a more profound manner with the halogenation products of the aldehydes of the mono hetero-atomic five membered rings than its original progenitor. With due consideration to the quantitative relationships and the time-temperature schedule, the ultimate reaction product will always be a partially dehalogenated reactive derivative. For convenience, these functional typical groups have been listed in alphabetical order:

Acetal	Boryl
Acetamido	Bromo
Acetimido	Carbonyl
Acid anhydride	Carbylamine
Acid halide	Carbonyldi-oxo
Alcoholic OH group	Chloro
Aldehyde group	Chloromercuri
Aldo	Cyano
Alkyl thio	Cyanid
Amide	Cyanate
Amidoxime	Diazo
Amino	Diazo-amino
Amine	Diazotate
Amoxy	Diazonium
Anilino	Diazoxy
Antimono	Dithio
Arseno	Disulfide
Arsenoso	Epoxy
Arsinico	Ester
Arsino	Ether
Arso	Ethylidene
Arsono	Ethylidyne
Arsylene	Ethynyl
Azimino	Ethynylene
Azido	Fluoro
Azino	Formamido
Azo	Formazyl
Azoxy	Guanido
Benzamido	Guanyl
Benzimido	Halogeno
Biphenylenediazo	Hydrazide

Hydrazo	Piperonylidene
Hydrazino	Propargyl
Hydrazo	Propenyl
Hydrazono	Propenylidene
5 Hydroxamino	Propronyl
Isonitroso	Propylidene
Imidazolyl	Pyrazolyl
Imino	Pyridyl
10 Iodo	Pyridylidene
Iodoso	Pyrimidyl
Iodoxy	Pyrrolyl
Isocyano	Pyrryl
Isodiazo	Selenino
Isonitro	Seleninyl
15 Isonitroso	Seleno
Isothiocyane	Selenocycano
Isoxazolyl	Selenonio
Keto	Selenocycano
Lactam	Selenyl
20 Lactide	Semicarbazido
Lactone	Silicono
Mercapto	Silicyl
Mercuri	Silicylene
Methionyl	Stannyl
25 Methylene	Stibarseno
Methylenedioxy	Stibinoco
Methylidyne	Stibino
Nitramino	Stibo
Nitrilo	Stibono
30 Nitro	Stiboso
Nitroso	Stibylene
Oxalyl	Sulfamino
Oxamido	Sulfinio
Oximido	Sulfinyl
35 Oxo	Sulfo
Oxy	Sulfonamide
Pentazyl	Sulfonic
Perthio	Sulfonyl
Phenetidimo	Sulfunic
40 Phenolic	Telluro
Phenylazo	Tetrazyl
Phenetyl	Theonyl
Phenoxy	Thiazyl
Phenyl	Thienyl
45 Phenylazo	Thio
Phenylenediazo	Thiocarbonyl
Phenylidene	Thiocyano
Phenylureido	Thiohydroxy
Phosphorseno	Thiol
50 Phosphazo	Thiono
Phosphinico	Thionyl
Phosphino	Triazeno
Phospho	Triazinyl
Phosphono	Triazo
55 Phosphoro	Triazolyl
Phosphorosio	Uramino
Phthalal	Ureido
Phthalamido	Ureylene
Phthalidene	Vinyl
60 Picryl	Vinylene
Piperidyl	Vinylidene
Piperonyl	Xanthyl

Many of the partially dehalogenated reactive derivatives are suitable for further reaction with other reagents and in this manner serve as intermediates for the production of a wide variety of materials. Many of these partially dehalogenated reactive derivatives are of interest from the standpoint of resins, plasticizers, softeners, paint, varnish and lacquer ingredients, extenders for resins and rubber, as compounding ingredients in the production of plastics, resins, synthetic rubbers, insecticides, pharmaceuticals, photographic chemicals, tannin materials, etc.

As may readily be seen from a study of the above representative list of compounds or classes of compounds with which the chlorinated furfural can be made to react, this latter compound is indeed possessed of an extraordinary reactivity. It is no exaggeration to say that this compound may be made to react with virtually all known organic compounds. This unusual reactivity is, of course, associated with the reactive functional groups that are present in the chlorinated furfural. This unusual reactivity is perhaps anticipatable from a consideration of the fact that even relatively highly stable substances such as ethyl chloride or monochlor benzene can, under appropriate conditions, be made to react or combine with other materials. On the other hand chlorinated furfural contains eight potentially reactive chlorine atoms besides probably containing two other functionally reactive groups (an aldehyde group and an alcoholic hydroxy group). Chlorinated furfural reacts with water or the moisture of the air and with alkaline materials such as ammonia or the alkali metal or alkaline earth oxides or hydroxides or with organic bases such as aniline or polyamino compounds, often in a very violent, almost explosive manner.

Partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings may be made by reacting the same with organic materials such as foodstuffs, dyestuffs, pharmaceuticals, tannin materials, photographic chemicals, fuel oils, organic waste products, animal and vegetable oils, turpentine, rosin, various resins of either the thermosetting or thermoplastic types, natural and synthetic rubbers, gums, silks, rayon, cellulose, wool, synthetic linear superpolyamides, e. g., "nylon," etc., provided that at least 25 per cent of the halide atoms remains in the resultant compound. It is desirable, though not essential, that the reaction product remain in a fusible condition.

A study of hundreds of the partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings has led the present inventors to conclude that on the whole the reactive derivatives represent complex mixtures containing two or more products. That this is so may be anticipated from a consideration of the fact that the halogenated aldehydes are polyfunctional in character so that if but a single reacting group participates in the reaction, it should be possible to bring into being a plurality of isomerically related compounds. When, for example, methanol reacts with chlorinated furfural so that the mean methoxy content corresponds to say three methoxy groups, there undoubtedly are present compounds that contain one or two methoxy groups on the one hand, and on the other hand, there probably are present compounds that contain more than three groups. In this simple case, if one were to consider the theoretical isomers, it is conceivable that in all such a derivative may contain well over a hundred distinct chemical compounds. Where a more complex reaction procedure is utilized, it is quite conceivable that the so-called reactive derivative comprises no less than a thousand distinct chemical entities.

From a utilitarian standpoint, the partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings are possessed of an extremely diversified field of usefulness.

The products per se can, by further reaction, be converted into "non-reactive" derivatives, which latter are of themselves possessed of a great field of utility.

The partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings are highly useful as "curing agents" for a wide variety of resins including phenol-formaldehyde resins, urea resins, melamine resins, etc. When a reactive derivative is mixed with one of the aforementioned types of resins, it cures, sets up, or hardens the same under the influence of heat to a state of infusibility or thermo rigidity. The reactive derivatives of the present invention can often advantageously be utilized in lieu of hexamethylenetetramine. An extremely wide range of cures can be procured through their use. It is found that a variety of metallic oxides, particularly red iron oxide and to a lesser extent, material such as zinc oxide, antimony oxide, etc., are effective catalysts in speeding up the cure reaction. The inclusion of reactive organic bodies such as nitrophenols, polybasic acids, and anhydrides, e. g., maleic acid, furfuryl alcohol, polyamino compounds, amino hydroxy compounds and poly phenols is often advantageous. One advantage of these reactive derivatives resides in the fact that they can be produced in such a wide variety of physical and chemical properties. In this wise, it is easy to procure a derivative that shall be compatible with or soluble in a given resin or resin solvent.

The partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings are extremely useful as curing agents for rubbers, particularly the synthetic variety. Thus, through their use synthetic rubbers are converted or cured to a vulcanized rubbery state without the use of the time-honored vulcanizing agent, sulphur, and without the use of any so-called vulcanization "accelerator." In many instances phenomenal results are procurable. Thus, the more powerful of the derivatives permit one to procure tensile strengths of in the order of 6,000 lbs./sq. in. with elongations of 500 per cent or better out of butadiene-acrylonitrile copolymer rubber (Hycar OR-15). Such vulcanized stock, besides being much stronger than a corresponding sulphur vulcanizate, is possessed of superior aging qualities and a vastly improved resistance to flex cracking and tearing. The strength of such vulcanizates is practically unaffected by high test aviation gasoline. Butadiene-styrene copolymer rubber, commonly known as Buna S, is also susceptible to vulcanization by these reactive derivatives and here too, in many instances, superior results manifest themselves. Various other types of synthetic rubbers such as the Thiokols, etc., are susceptible to conversion to a vulcanized rubbery state by the use of these reactive derivatives. Fillers, lubricants, pigments, dyes, plasticizers, softeners, extenders, modifiers, and other rubber compounding ingredients may be included in the formulations.

The partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings are endowed with the remarkable attribute of being able to cure or convert to a thermo rigid or vulcanized rubbery state organic polymers containing a plurality of hydroxy (OH) groups. Typical of such hydroxylated polymers are those

described in copending application, Serial No. 464,896, filed November 7, 1942, now abandoned.

It thus becomes possible through the use of the herein described reactive derivatives to convert to a thermo rigid or vulcanized rubbery state after appropriate hydroxylation, nominally heat non-convertible polymers, element convertible polymers, linear polymers, addition or "A" polymers, three dimensional polymers, and addition or "C" polymers. Specifically through the use of the reactive derivatives, it becomes possible to cure to a thermo rigid or vulcanized rubbery state hydroxylated polymers derived from polycoumarones, polyindenes, polystyrenes, polyacrylates, polymethacrylates, polyolefines, polyoxymethylenes, polyvinyls, e. g., polyvinyl organic esters, polyvinyl inorganic esters such as polyvinyl chloride, vinyl copolymers, polyvinyl ethers, polyvinyl acetals, etc., phenol-aldehyde resins of the Novolak type, permanently thermoplastic alkyd resins, e. g., dihydric alcohol-dibasic acid resins, resinous or rubbery acetylene polymers, resinous or rubbery hydrocarbon polymers, resinous or rubbery petroleum polymers, and ethylene polymers, etc. Of equal utility are the hydroxylated products derivable from the aforementioned products but which contain halide, i. e., chlorinated polymers, e. g., chlorine containing polycoumarones, chlorine containing polyindenes, chlorine containing polystyrenes, chlorine containing polyacrylates, chlorine containing polymethacrylates, chlorine containing polyolefines, chlorine containing polyoxymethylenes, chlorine containing polyvinyls, e. g., chlorine containing polyvinyl organic esters, chlorine containing polyvinyl inorganic esters such as chlorine containing polyvinyl chloride, chlorine containing vinyl copolymers, chlorine containing polyvinyl ethers, chlorine containing polyvinyl acetals, etc., chlorine containing phenol-aldehyde resins of the Novolak type, chlorine containing permanently thermoplastic alkyd resins, chlorine containing resinous or rubbery acetylene polymers, chlorine containing resinous or rubbery hydrocarbon polymers, chlorine containing resinous or rubbery petroleum polymers, and chlorine containing ethylene polymers, etc. The hydroxylated products derived from polymeric substances resulting from chlorination followed by dechlorination either prior or subsequent to the polymerization are equally suitable. Often the inclusion of reactive organic bodies such as polyalcohols, polyamino compounds, amino hydroxy compounds, amino acids, amides, furfural, furfuryl alcohol, methyl furfuryl alcohol, natural rubber vulcanization accelerators, etc., is desirable. Sometimes the inclusion of inorganic materials as typified by red iron oxide, zinc oxide, aluminum oxide, antimony oxide, manganese dioxide, etc., is beneficial. Polyvinyl alcohols, polyvinyl alcohol-acetate polymers, and polyvinyl acetals such as polyvinyl butyral are very readily cured by the use of these reactive derivatives.

The products of the present invention are able to effect a cure of all manner of polyamino polymers whether they be resinous or rubbery in nature. Included in this category are substances akin to those mentioned in the preceding paragraph, but which in lieu of the hydroxy (OH) groups contain amino groups which may be primary, secondary or in part at least, even tertiary. Substances such as glues, albuminoids, proteins, including modified casein products and modified resinous or rubbery products derived from proteins are susceptible to reaction with the

herein described partially dehalogenated reactive derivatives.

The reactive derivatives described in the present invention are of utility in elevating the softening point of nominally thermoplastic products. Thus, by the judicious use of selected types of reactive derivatives or their use along with an appropriate coreagent, it is possible to elevate the softening point of polyvinyl acetate plastics, polyvinyl chloride plastics, polystyrene plastics, etc., etc. The products of the present invention are also extremely useful in that they bring about a species of "cure" of cellulosic products including the cellulose ethers, cellulose esters, etc. (e. g., cellulose nitrates, cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetobutyrate, cellulose esters of dibasic acids, methyl cellulose, ethyl cellulose, propyl cellulose, butyl cellulose, etc.). Such products can be appreciably "insolubilized" via the use of the products of the present invention.

The reactive derivatives are usable for the manufacture of resins from such diverse products as phenols, amines, polyamines, as well as a wide variety of naturally occurring substances including vegetable and animal oils, fats, waxes, gums, resins, etc.

The reactive derivatives permit the production of an almost limited number of chemical intermediaries which are useful for the manufacture of curing agents, vulcanizing agents, accelerators, antioxidants, dyestuffs, photographic chemicals, synthetic tannin materials, pharmaceuticals, insecticides, etc., etc.

The partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings are useful in the preparation of impregnating materials, floor coverings, coatings, paints and varnishes, cements, bonding agents, etc. When used for these purposes, the reactive derivative may function as a curing aid, as a component of a resin structure, a plasticizer or as a modifying agent.

The partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings constitute a unique and distinct class of substances. The materials may be variously characterized. Thus, they may be characterized as to their derivation inasmuch as the only known means whereby these materials can be synthesized is by way of the halogenation products of the aldehydes of the mono hetero atomic five membered rings. They are further characterized in that they retain not less than 25 per cent of the original halide atoms contained in the saturated halogenated aldehydes from which they are derived. The products of the present invention can also be characterized in terms of their reactivity. Thus, they all enter into reaction with substances such as tetraethylene pentamine.

It is thought to be clear from the foregoing disclosure that the partially dehalogenated reactive derivatives of the halogenation products of the aldehydes of the mono hetero atomic five membered rings, and particularly the derivatives of chlorinated furfural and its immediate homologues and analogues constitute a novel and unique class of chemical substances possessed of an extremely wide range of chemical and physical properties and having an exceedingly wide range of industrial applications. The reactive derivatives are useful in the manufacture or prepara-

tion of such varied products as the following—for convenience listed alphabetically:

Abrasive articles	Lamp basing cements
Acidic catalysts	Leather substitutes
Acidic reactants	Lacquers
Adhesives	Molding compositions
Analytical reagents	Paints
Bactericides	Pharmaceuticals
Brake linings	Photographic chemicals
Cements	Plasticizers
Chemical intermediaries	Plastics
Chemicals for the paper industry	Plywood
Cleansing agents	Poisons
Coupling agents	Printing plate matrixes
Curing agents	Printing plates
Dyestuffs	Proofings to water, oil, etc.
Electrical insulation	Repellents
Enamels	Resins
Explosives	Rubber substitutes
Extenders for resins, plastics, rubbers, etc.	Rubber vulcanization accelerators
Fillers for resins, rubbers, etc.	Rusting agents
Floor coverings	Solvents
Frictional elements	Stiffening agents
Frictionings	Synthetic and natural rubbers
Fungicides	Synthetic fibers
General reactants	Tanning agents
Germicides	Textiles
Glues	Ultra reactive co-reactants
Gums	Varnishes
Hardening agents	Vesicants
Impregnating agents	Vulcanizing agents
Inks	
Insecticides	

The invention has been described in connection with a number of illustrative embodiments, materials, proportions, conditions and arrangements of operations for carrying out the invention. It is, therefore, to be understood that the invention is not to be restricted to the foregoing disclosure, and that no limitations are to be imported required by the language of the appended claims and the state of the prior art. It is further to be understood that the invention is not dependent upon any explanations or theories which have been set forth as descriptive of the actions involved, nor dependent upon the accuracy or soundness of any theoretical statements so advanced.

We claim:

1. The method of producing reactive halogen containing organic compounds which consists in dehalogenating substantially fully saturated halogenation addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average halogen content of the resultant partial dehalogenation product is equal to not less than one atom of halogen per molecule of aldehyde that entered into the making of the aforesaid saturated halogenation addition product.

2. The method of producing reactive chlorine containing organic compounds which consists in dehalogenating substantially fully saturated chlorination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average chlorine content of the resultant partial dehalogenation product is equal to not less than one atom of chlorine per molecule of aldehyde that entered into the making of the aforesaid saturated chlorination addition product.

3. The method of producing reactive bromine containing organic compounds which consists in dehalogenating substantially fully saturated bromination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average bromine content of the resultant partial dehalogenation product is equal to not less than one atom of bromine per molecule of aldehyde that entered into the making of the aforesaid saturated bromination addition product.

4. The method of producing reactive iodine containing organic compounds which consists in dehalogenating substantially fully saturated iodination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average iodine content of the resultant partial dehalogenation product is equal to not less than one atom of iodine per molecule of aldehyde that entered into the making of the aforesaid saturated iodination addition product.

5. Reactive halogen containing organic compounds produced by the method which consists in dehalogenating substantially fully saturated halogenation addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average halogen content of the resultant partial dehalogenation product is equal to not less than one atom of halogen per molecule of aldehyde that entered into the making of the aforesaid saturated halogenation addition product.

6. Reactive chlorine containing organic compounds produced by the method which consists in dehalogenating substantially fully saturated chlorination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average chlorine content of the resultant partial dehalogenation product is equal to not less than one atom of chlorine per molecule of aldehyde that entered into the making of the aforesaid saturated chlorination addition product.

7. Reactive bromine containing organic compounds produced by the method which consists in dehalogenating substantially fully saturated bromination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average bromine content of the resultant partial dehalogenation product is equal to not less than one atom of bromine per molecule of aldehyde that entered into the making of the aforesaid saturated bromination addition product.

8. Reactive iodine containing organic compounds produced by the method which consists in dehalogenating substantially fully saturated iodination addition products of the aldehydes of the monoheteroatomic five membered rings to a point where the average iodine content of the resultant partial dehalogenation product is equal to not less than one atom of iodine per molecule of aldehyde that entered into the making of the aforesaid saturated iodination addition product.

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