

This invention relates to new mouldable, radically polymerizable multicomponent mixtures which are used, for example, as free-flowing or spreadable compositions or as pastes and then cured under ambient conditions through
5 initiation of the polymerization reaction. In application-
al terms, the invention relates in this regard to almost
any field where radically polymerizable or curable compositions are used, including for example adhesives, sealing
compounds, the specific production of plastics mouldings,
10 surface coating with air-curing and, in particular, solventless paint systems and the like.

The peroxide- or hydroperoxide-initiated curing of olefinically unsaturated systems requires activator systems made up of several components, particularly when the reaction is to be initiated at low temperatures, for example at
15 room temperature or only slightly elevated temperature. It is known that selected tertiary amine compounds partly aromatically substituted at the nitrogen atom perform such an activating function. Known activators for the initiation of polymerization reactions by benzoyl peroxide, for
20 example, are in particular dimethyl aniline and dimethyl-p-toluidine.

A totally different known class of activators for oxidative initiation of the polymerization of certain unsaturated systems, namely drying oils, are metal compounds
25 - at least partly soluble in the system - of metals which can occur in several valency stages and accelerate the initiating reaction through intermediate shifts in valency on interaction with other components of the system. Metal
30 compounds such as these - sufficiently soluble in organic solvents and/or in binders - of metals of the type in question have long been known as so-called dryers for the air drying of paints, varnishes and the like based on unsaturated oils. Sufficiently oil-soluble compounds of transition
35 metals, which are capable of occurring in several

valency stages, are particularly suitable for this purpose. The individual components differ in their ability to accelerate curing, compounds of cobalt and/or manganese being particularly suitable, although iron also accelerates curing. In addition to and, in particular, in combination with these highly active metallic components, it is possible to use comparable compounds of other metals which may also be capable of forming several valency stages. A detailed description of such systems can be found, for example, in "Ullmann, Encyklopädie der technischen Chemie", 4th Edition, Vol. 23 (1983), 421-424.

It is also known that the two types of promoters described here for the radical initiation of polymerization can lead by interaction to an enhanced effect. For example, the Article by L. HORNER et al "Autoxidationsstudien an N,N-dialkylierten Anilinderivaten (Autoxidation Studies on N,N-Dialkylated Aniline Derivatives", in Makromolekulare Chemie 93 (1966), 69 to 108, relates to investigations into the acceleration of the spontaneous autoxidation of N-dialkyl-substituted arylamine compounds in pure, highly dry oxygen gas. In the first stage of the spontaneous autoxidation, the amine hydroperoxide compound is formed at aliphatic CH groups in the α -position under the effect of dried, superpure oxygen. This spontaneous autoxidation of the N,N-dialkylated arylamines takes place very slowly. According to the Article in question, the co-use of cobalt(II) compounds and, to a lesser extent, the co-use of iron(III) salts results in activation of the autoxidation process. In further studies reported in this Article, it is shown that acetic acid also has a pronounced accelerating effect on autoxidation at the tertiary amine compound whereas stronger acids, such as trichloroacetic acid, or mineral acids form true tertiary ammonium salts which are not autoxidizable. The use of cobalt ions in conjunction with acetic acid leads to the vigorously catalyzed autox-

idation of dialkyl aniline compounds under the effect of superpure oxygen.

Finally, the Article cited above describes studies into the initiation of the polymerization of vinyl compounds by the dimethyl aniline/superpure oxygen/cobalt salt system. High-purity acrylonitrile, methyl methacrylate, ethyl acrylate and styrene can be polymerized with this system. The initiating reaction is interpreted as redox catalysis in which molecular oxygen acts as oxidizing agent. There are no references in the publication in question to the suitability of the multicomponent systems investigated for practical use in the polymerization field. In fact, however, these theoretical works, which have been available to experts for almost 25 years, have not provided any encouragement for their practical application.

The problem addressed by the present invention is to utilize existing knowledge of multicomponent redox systems as described above in providing a new class of activator systems which may be used in a new and simplified way for initiating the polymerization of olefinically unsaturated systems. The new activator systems are intended to lead in the absence of oxygen and water to non-reactive mixtures which do not polymerize in admixture with the olefinically unsaturated, polymerizable components and are therefore stable in storage both in the form of one-component systems and also in the form of multicomponent systems. On the other hand, the new activator systems are intended to be able to be activated by the action of water and oxygen. In preferred embodiments, this activation is intended to take place even at room temperature, although a moderate increase in temperature may be necessary. A particularly important aspect of the invention relates to multicomponent systems of the above-mentioned type which, by virtue of the moisture and oxygen always present in them, are capable of initiating the starting reaction of a radical polymeriza-

tion of unsaturated systems at room temperature or only moderately elevated temperatures simply by contact with ambient air.

In a first embodiment, therefore, the present invention relates to mouldable, radically polymerizable multi-component mixtures containing

- ethylenically unsaturated, polymerizable compounds, if desired in admixture with soluble and/or insoluble fillers and
- 10 - an activator system initiatable by contact with oxygen,

characterized in that these multicomponent mixtures contain an activator system based on the following principal components which can be initiated by contact with oxygen and water and, in particular, by contact with ambient air:

- N-alkyl-substituted tert.-arylamines containing at least one aliphatic CH bond in the α -position
- metal compounds at least partly soluble in the system to accelerate the drying of unsaturated oils and
- 20 - compounds of weakly acidic carboxylic acids having pK_s values of no less than about 0.9 which can be hydrolyzed to the free carboxylic acid on contact with moisture.

Accordingly, the essence of the teaching according to the invention lies in the choice of the specific activator system which is being described for the first time in this combination. This system differs from the activator systems described by L. HORNER et al. in particular in the choice of the third component described above. According to the invention, the free carboxylic acid is not present as such, as in the case of the acetic acid investigated by HORNER, but instead in the form of carboxylic acid derivatives which, as such, do not contain any free carboxyl groups, but can be hydrolyzed to the free carboxylic acid on contact with moisture. Accordingly, the simplifications

and extended applications thus created in practice immediately become clear.

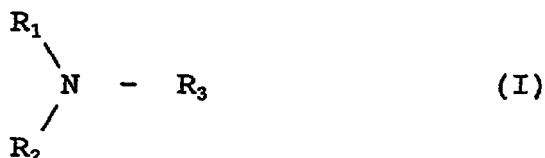
The state of activation required for the initiation of polymerization in the context of the invention requires the cooperation of the aromatic amine and the metal compound at least partly soluble in the system with the free carboxylic acid. However, because the free carboxylic acid is not introduced as such, but instead in masked form, an additional degree of freedom is created in regard to inhibition of the system as a whole. It is known that the complete absence of oxygen or rather the corresponding elimination of oxygen from multicomponent mixtures cannot be reasonably achieved in practice. Starter systems which convert molecular oxygen into a reaction-initiating intermediate stage - or polymerizable mixtures containing such starter systems - are always comparatively jeopardized by unwanted secondary reactions. The possibility which the invention affords of additionally inhibiting the system by the absence of moisture increases safety during the production, handling, storage and use of the air-sensitive systems. The freedom created in this regard can be further increased by suitable auxiliary measures described in the following. In particular, it is also possible in this way to produce and store the polymerizable compounds as a non-reactive one-component mixture. Mere contact with air at ambient temperature or at most moderately elevated temperatures is sufficient to activate the starter system and, hence, to initiate the reaction in the system as a whole for dimensionally stable curing. The open time of the system required for moulding may be varied within wide limits through further measures proposed in accordance with the invention, as described hereinafter. Practical significance is thus attributed to multicomponent systems having the composition according to the invention in the broadest applicational sense.

The three main components of the activator system used in accordance with the invention will first be described in detail in the following:

5 N-alkyl-substituted tert.arylamines

All corresponding compounds containing at least one aliphatic CH bond in the α -position are suitable. The amine components used in accordance with the invention correspond in particular to general formula I:

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in which

R_1 is an optionally substituted aryl radical, R_2 has the same meaning as R_1 or may even be an optionally substituted alkyl radical. This alkyl radical may be linear or branched. R_3 is a linear or branched alkyl radical which may even be substituted and which may be the same as or different from the alkyl radical optionally present in R_2 , but is always distinguished by the fact that at least one H atom is present in the α -position to the N.

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The preferred aryl radical is the phenyl radical which may even be substituted, more especially alkyl-substituted. The alkyl radicals present in R_3 and optionally R_2 each preferably contain up to about 10 carbon atoms and, in particular, up to about 6 carbon atoms. Particular significance is attributed to corresponding C_{1-3} radicals and again to the methyl radical in particular. In one preferred embodiment, the radicals R_2 and R_3 are corresponding, optionally substituted alkyl radicals while the radical R_1 is an optionally substituted phenyl radical, so that N,N-dialkyl-substituted aniline compounds, which may also be alkylated in the phenyl ring, are generally preferred. The

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most important components in the context of the invention are dimethyl aniline and, in particular, dimethyl-p-toluidine.

Basically, the principles stated by L. HORNER et al.,
5 loc. cit., apply to the activity and the activatability of these tertiary amine compounds: nucleus substituents influence the autoxidation rate of the dimethyl aniline. Electron donors increase the autoxidizability of the amine, electrophilic substituents reduce it. Accordingly, p-
10 toluidine compounds are more reactive than the otherwise structurally identical aniline derivatives. The general principles stated by HORNER also apply with regard to the alkyl substituents in R_3 and R_2 . The methyl group is far more accessible to oxidation to the hydroperoxide than all
15 other N-alkyl substituents. Basically, the known results of the action of dibenzoyl peroxide on tertiary amines, as reported in the cited literature reference, also apply here.

20 Metal compounds at least partly soluble in the system

As already mentioned, the most important dryers of the type in question are distinguished by the fact that, above all, metal compounds of metals capable of occurring in several valency stages are used. Selected representatives
25 of the transition metals can be particularly active in this regard. The particular choice of the metal may have inter alia a velocity-determining effect on the initiation of polymerization on account of a certain dependence on temperature of the reactive intervention of this metal compo-
30 nent in the process as a whole. Components which are highly active at room temperature are derived in particular from cobalt and/or manganese. Iron also has a certain, albeit weaker, effect in accelerating the reaction at room temperature. The activity of other metal components, for
35 example those based on vanadium, can be increased by

increasing the temperature to such an extent that the polymerization reaction can be rapidly initiated.

Cobalt and/or manganese compounds, optionally in admixture with other metallic components, such as compounds of lead, cerium, calcium, barium, zinc and/or zirconium, are particularly suitable for working at room temperature which is of particular advantage for numerous applications. Reference is made in this regard to the relevant specialist literature, cf. for example the cited publication in "Ullmann" loc. cit. and the literature cited therein.

The metals in question here are used in the form of such compounds that they are at least partly soluble in the system as a whole. Both soap-like metal compounds and also types attached otherwise, particularly in complex form, to organic radicals are suitable. A typical example of working in accordance with the teaching of the invention is the use of corresponding metal naphthenates or metal acetylacetonates. Providing inorganic salts are sufficiently soluble in the system, it is also possible to use such inorganic systems. A typical example is iron chloride which has a distinctly accelerating effect when used in the system according to the invention.

It may be advisable to use the metal compounds in a low valency stage of the metal, i.e. for example as cobalt-(II) or manganese(II). In other cases, it is also suitable to use the metal compound in the higher valency stage of the metal. Thus, iron chloride, for example, is preferably used in the form of the Fe^{3+} salt.

Masked carboxylic acid compounds hydrolyzable on contact with moisture

A factor of crucial importance in the selection of these components is the acidity of the free carboxylic acid. The pK_s value of the free acid should be no lower than about 0.9, the preferred limit being at about 1.

If much more strongly acidic components are used, acceleration of the reaction comes to a stop. This is illustrated by the following examples. The pK_s value of trichloroacetic acid is approximately 0.6. The addition of
5 trichloroacetic acid in masked or unmasked form to the system destroys the ability of the multicomponent initiator system used in accordance with the invention to initiate polymerization reactions. By contrast, dichloroacetic acid is a relatively weak carboxylic acid with a pK_s value of
10 approximately 1.3. This dichloroacetic acid is eminently suitable for initiating polymerization reactions in accordance with the invention. Strongly acidic mineral acids, for example hydrochloric acid, also affect the ability of the activator systems used in accordance with the invention
15 to initiate polymerization reactions. Acetic acid or derivatives hydrolyzable to acetic acid (pK_s value of acetic acid approx. 4.76) are eminently suitable for accelerated reaction initiation.

The upper limit to the pK_s value may be seen in the
20 region of very weakly acidic compounds - determined as free carboxylic acid. In numerical terms, therefore, the upper limit is at pK_s values of approximately 13 and, preferably, at pK_s values of approximately 11.5. However, carboxylic acids which have pK_s values in the hydrolyzed state of up to
25 about 8 and preferably of up to about 6 or 7 are particularly suitable. Particularly effective components of the type in question here are thus derived from carboxylic acids which have pK_s values in the hydrolyzed state in the range from about 1 to 6 or 7.

30 The carboxylic acids to be used in masked form in accordance with the invention may contain one or more carboxyl groups. The constitution of the acid as such is not such a crucial parameter given the correct pK_s value. So far as the practical application of the invention is
35 concerned, the reliable availability of the fully masked

form of the particular carboxylic acid is the prime consideration. In the preferred embodiment of the invention, steps are taken to ensure that no free carboxyl groups are present in the starting mixture, but are only formed during processing by hydrolytic elimination of the masking part of the molecule. In preparative terms, therefore, it can be of advantage for the component in question here to be based on carboxylic acids containing 1 to 4 carboxyl groups and, in particular, 1 or 2 carboxyl groups. It may be particularly simple to use masked monocarboxylic acids because the need to eliminate free carboxyl groups can be satisfied particularly easily in their case. The choice of the particular carboxylic acid is also largely determined by corresponding expediency considerations. Readily obtainable carboxylic acids, such as lower aliphatic carboxylic acids or corresponding aromatic mono- or polybasic carboxylic acids are suitable components. Suitable aliphatic carboxylic acids are C_{1-18} and preferably C_{1-10} monocarboxylic acids, acetic acid again being particularly important. Suitable aromatic carboxylic acids are benzoic acid or corresponding polycarboxylic acids, for example trimellitic or pyromellitic acid. As shown with reference to the example of dichloroacetic acid, substituted acids of this type are also suitable providing their pK_s value is within the stated limits. It is crucial to the teaching according to the invention that these weak carboxylic acids be used in the form of their hydrolysis-labile derivatives. Particularly suitable derivatives are corresponding derivatives of weakly acidic carboxylic acids corresponding to general formula II



in which R_4 is an optionally substituted alkyl, cycloalkyl or aryl radical and X is a weakly acidic, substantially

neutral or, in the extreme case, very weakly basic radical removable by hydrolysis at at most slightly elevated temperatures with simultaneous formation of the free acid R_4COOH . This limitation in the definition of the radical X ensures that the weak acid R_4COOH can actually perform the reaction-initiating function assigned to it. Suitable hydrolysis-labile derivatives of the weak carboxylic acids are, for example, their anhydrides or their mixed anhydrides with other weak carboxylic acids, these other weak carboxylic acids in particular also meeting the requirements stated above in regard to the pK_s limit. Particularly suitable derivatives of the type in question are mixed anhydrides or esters of the weak carboxylic acids used in accordance with the invention with hydroxy compounds of hetero atoms which, after hydrolysis, do not affect the acidity level in the system according to the invention. The mixed anhydrides or esters with corresponding compounds of boron and/or silicon described hereinafter are particularly suitable in this regard.

The velocity of the reaction can be influenced through the hydrolysis stability of the masked carboxylic acid compound used. This opens up possibilities of influencing the reaction to enable the course of polymerization to be adapted to the particular application envisaged. This is explained purely by way of example in the following. A masked carboxylic acid compound in the context of the invention is acetic anhydride. However, acceleration of the reaction during initiation of polymerization by molecular oxygen, more especially by contact with air, is only brought about by free acetic acid after adequate hydrolysis. This hydrolysis of the anhydride in situ in the reaction mixture at room temperature under the effect of air with its limited moisture content can be a comparatively laborious process. On the one hand, the open time of the reactive system is lengthened in this way, on the other

hand setting of the reactive system can be unreasonably delayed in individual cases. If comparatively more hydrolysis-labile compounds, for example of the type described hereinafter, are used instead, the system as a whole is effectively activated in only comparatively short times. Taking this consideration into account, the following meanings in particular may be attributed to the radical X in general formula II:

radicals corresponding to general formula III



in which R_5 may be the same as or different from R_4 in general formula II and, in particular, represents alkyl, cycloalkyl or aryl; all these radicals may also be substituted with the proviso that the free carboxylic acid R_5COOH formed during hydrolysis corresponds at least to the above-mentioned lower limit to the pK_s value.

Mixed anhydrides or esters with boron compounds containing hydroxyl groups are suitable as comparatively hydrolysis-labile components. In this class of compounds, the radical X in general formula II preferably corresponds to the radical of general formula IV below

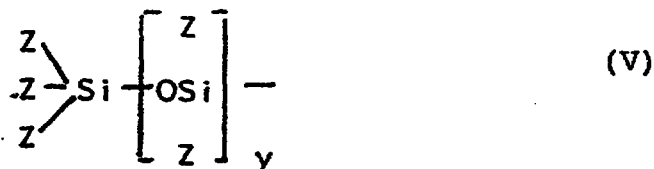


In that part of the molecule which corresponds to general formula IV above, the Z's may be the same or different and, in particular, represent a radical $R_5-CO-O-$ and/or alkyl, cycloalkyl and/or aryl radicals which in turn may optionally be substituted and/or attached to the boron by an oxygen atom. R_5 has the meaning already defined in connection with general formula III. x is 0 or an integer and,

in particular, has a value of 0 to 2. A particularly important masked, weak carboxylic acid for use in accordance with the invention is derived from compounds corresponding to general formula II, in which X is a radical
 5 corresponding to general formula IV where x is the number 1 and the Z's represent $R_4\text{-CO-O-}$. A typical representative of this class of compounds is tetraacetoxo diboroxane which has proved to be a particularly effective carboxylic acid compound and which is easy to prepare and to mask in
 10 readily stabilized form, but can be rapidly hydrolyzed on contact with ambient air.

Another particularly suitable class of these masked carboxylic acid compounds is derived from analogous compounds of silicon in the radical X. Compounds of this type
 15 also correspond to general formula II although, in their case, X has the meaning defined by general formula V below:

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25 where Z can have the same meaning as in formula IV and y preferably has a value of 0 to about 10 and, more preferably, a value of 0 to about 5. For preparative reasons, it may be advisable for the radicals Z in compounds of this type to be formed by hydrocarbon radicals and, in particular,
 30 lar, by alkyl radicals, more especially lower alkyl radicals, such as methyl. In one preferred embodiment, at least two alkyl radicals, particularly methyl radicals, are present in that part of the molecule which corresponds to general formula V at at least some silicon atoms and
 35 preferably at all the silicon atoms. Components of this type are particularly easy to prepare so that the associ-

ated masked compounds of general formula II are particularly easy to obtain.

Certain integral components may be present as compounds of general formula II, in which X corresponds to
5 general formula IV or V in regard to the indices x and y, as already explained in regard to the case of tetraacetoxy diboroxane. However, it is also possible to use homologous mixtures in regard to the radicals IV and particularly in regard to the radical V, so that x and, in particular, y as
10 average values do not have to correspond to integral values.

Activator systems of the three principal components described in the foregoing, namely aromatic amine compound, at least partly soluble metallic dryer and masked weak acid
15 capable of hydrolysis, are able after taking up moisture and oxygen from the ambient air to initiate all the radically polymerizable, olefinically unsaturated systems which, hitherto, have been used with a variety of different, particularly peroxidic, starter systems. To this
20 extent, the other constituents of the radically polymerizable, mouldable multicomponent mixtures according to the invention may be as defined in the extensive relevant literature which is concerned with the production and processing of systems based on olefinically unsaturated
25 radically polymerizable compounds. A very large number of systems of this type tailored in their properties to the particular application envisaged are currently available to the expert. Basically, the principle according to the invention of initiating reactions by contact with oxygen
30 and particularly by mere contact with ambient air may be applied anywhere where there is no possibility of troublesome interaction with the above-described principal components of the activator system used in accordance with the invention. General chemical knowledge in conjunction with
35 the above-described principles of the teaching according to

the invention will be sufficient to determine the extent to which specially selected systems can be used or how they have to be used in the context of the invention to meet the requirements of the teaching according to the invention.

5 This is illustrated by the following example:

Polymerizable components and, optionally, soluble and/or insoluble fillers and also the mixtures containing activator systems according to the invention may be formulated as a one-component system which is non-reactive in
10 the absence of air providing measures are taken to ensure that the mixture does not contain any constituents which lead to the unwanted premature reaction of at least one of the principal components of the system according to the invention. Thus, for the formulation of one-component
15 systems, it is particularly important that the systems as a whole are free from reactive groups, particularly in the form of reactive hydrogen atoms, as present for example in the form of hydroxyl and/or carboxyl groups. Reactive groups such as these containing active hydrogen atoms are
20 always troublesome when they lead to premature release of the masked, weakly acidic carboxylic acids.

However, the presence of reactive groups such as these in no way makes it impossible to use the starter systems according to the invention. For example, this affords the
25 possibility of using the multicomponent system. If, for example, components containing active hydrogen atoms, for example in the form of free carboxyl and/or hydroxyl groups, are to be used in the system as a whole, the multicomponent mixture to be used in accordance with the invention may be formulated as a multicomponent system in this
30 embodiment. In this case, it is important to ensure that the components containing reactive hydrogen atoms are kept separate from the masked, weak carboxylic acids of the activator system according to the invention in the multicomponent system. For the practical application of the
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system, the components are mixed with one another in known manner. The open pot life of the system may be regulated by suitable choice and adaptation of the principal components of the activator system, so that the starting reaction can again be initiated and, hence, the system ultimately cured by contact with ambient air. This purely exemplary explanation of using components containing reactive hydrogen atoms also applies to other reactive components. Providing the activator system remains functional even after all the components of the multicomponent mixture have been mixed together, its suitability for use under the described conditions is guaranteed.

Another way of removing potentially reactive and hence troublesome groups from the reaction is to mask them. This principle, which applies to another preferred embodiment of the invention, is illustrated with reference to the example of unwanted free carboxyl groups. By temporary masking with, for example, groups unstable to hydrolysis, it is possible to ensure that no unwanted secondary reactions are initiated during storage in the absence of moisture. However, the masking of such free carboxyl groups can be removed again at a later stage by the action of moisture which is required in any event for initiating reactions. However, it is possible in this regard to regulate the stability of the masked form through the degree of instability to hydrolysis. General chemical principles apply in this regard. This principle of the hydrolysis-labile masking of free carboxyl groups may also be applied in particular in the following combination: important olefinically unsaturated and radically polymerizable acids, such as (meth)acrylic acid(s), crotonic acid, maleic acid and the like, may be added to the reaction mixture and hence to the reaction in this masked form. If the masking of these acid components is more stable to hydrolysis than the masked carboxylic acid component - added to initiate

reactions - of the activator system used in accordance with the invention, the unsaturated carboxylic acids will initially be included in the polymerization process in masked form. The masking may be eliminated by hydrolysis at a later stage. However, it is clear that it is also possible in accordance with the invention at least partly to use unsaturated carboxylic acids such as these in masked, but hydrolysis-labile form as a weakly acidic catalyst component. In this case, a dual reaction-initiating function is performed, for example, by the acrylic or methacrylic acid in the reaction mixture. After adequate hydrolytic elimination of the masking, the free acid formed has a reaction-initiating effect in cooperation with the other components of the activator systems according to the invention, but at the same time is included in the polymerization process and bound into the polymer molecule formed.

In one particular embodiment, the invention relates to multicomponent systems which are non-reactive, even on contact with air, and only initiate the starting reaction required in accordance with the invention after all the components have been mixed. This embodiment is based in particular on the division of the activator system into a two-component system. In the preferred embodiment, the tert.N-compound is kept separate from the metal compounds and the compounds hydrolyzable to free carboxylic acids. However, both components of the system as a whole may contain substantial proportions of the compounds to be polymerized and/or the other fillers and auxiliaries to be used. In this case, it is possible in particular to distribute the quantities of the principal components of the multicomponent mixture between the two components in such a way that both individual components make up substantial proportions of the mixture as a whole. In this way, it is possible during dosing and mixing to form the ready-to-use mixture to avoid the difficulties which can occur

for example when a component kept separate in only a very small quantity is to be quickly and reliably distributed in a very large quantity of a second component.

In the preferred embodiment, the multicomponent mix-
5 tures according to the invention, which contain both the activator system according to the invention and the components to be polymerized in admixture with their fillers and/or auxiliaries, are formulated as a free-flowing, but at least slightly thickened to paste-like and spreadable
10 multicomponent mixture. The particular consistency intended is adapted to the application envisaged. Adhesives and filling or sealing compounds will generally be given a more paste-like consistency than spreadable or sprayable paints. In one preferred embodiment, the systems are free from
15 solvents. Their flow properties are generally adjusted or regulated by ethylenically unsaturated monomers. At the present time, the monomers predominantly used in the field of radically initiated polymerization are based on acrylate and/or methacrylate compounds, styrene or substituted
20 styrenes and/or acrylonitrile. The activator systems according to the invention are effective initiators for monomers of this type, particularly in the systems typically used at present, and may be formulated in particular as initiators reacting on contact with ambient air at room
25 temperature or only slightly elevated temperatures. The initiation of polymerization reactions in accordance with the invention may be applied to the entire range of known acrylate or (meth)acrylate systems and styrene-modified mixtures and particularly to systems based on unsaturated
30 polyester resins/styrene.

It has been found that polymerisation reactions can be rapidly and effectively initiated at the time determined in advance for the particular system in question when the systems used have at least slightly elevated viscosity
35 values. Thus, the initiation of polymerization above all

in the pure unsaturated monomer stabilized in the usual way, for example in commercially available pure (meth)acrylate, styrene and the like can present difficulties. However, if these components are even only slightly thickened, polymerization can be initiated without difficulty by contact with ambient air. The minimum viscosity of the systems to be cured in accordance with the invention in the in-use state is at least about 30 to 100 mPas (Brookfield). It may be appropriate to work with slightly higher viscosities in the original processing state so that preferred limits are at about 200 mPa.s and, more particularly, at at least about 300 mPa.s. Materials with viscosities of at least about 500 are often of particular practical significance; this applies not only to adhesives and sealing compounds with viscosities above about 3000 mPa.s and, more particularly, of up to about 10,000 mPa.s, but also to mixtures intended for surface coating, particularly solventless paint systems. In cases of practical relevance, there is generally no need to regulate the minimum viscosity. Only in the special case of highly mobile liquid phases, as formed for example by the unsaturated monomers mentioned above, need appropriate auxiliary measures be considered for slightly thickening the system.

The possibility of formulating one-component systems which are non-reactive in the absence of air and which react under time control on contact with air enables the scope of potential technical applications to be considerably extended. This is illustrated by the following example:

Ready-to-use one-component adhesives based for example on methacrylate, which cure simply by contact with air to initiate polymerization, are not known. The only adhesive system which has been formulated for practical application in accordance with this ideal are the cyanoacrylate adhesives which, however, are attended by considerable prac-

tical difficulties. The reaction on which the curing of cyanoacrylate adhesives is based takes place under the effect of moisture by an anionic mechanism; the stability of such one-component materials in storage is always
5 seriously jeopardized. The performance of cyanoacrylates as adhesives is limited by their limited physical properties.

By contrast, the invention provides for the formulation of optimized acrylate- and/or methacrylate-based adhesive mixtures in the form of a non-reactive one-component
10 mixture which is activated and thus tackified by application to the surfaces to be bonded and the accompanying exposure to ambient air and subsequently cured. Without departing from the principles of the invention, including
15 in particular inert behaviour with respect to the main components of the activator system, it is possible to use soluble and/or insoluble fillers, elasticizers, thickeners, thixotropic agents, pigments, coupling agents, stabilizers and the like without endangering the performance of the
20 activator system according to the invention.

One particular feature of the multicomponent mixtures according to the invention or rather the activator systems used therein is that double inhibition and hence double control of the system as a whole is possible. Through the
25 presence of dryers, the multicomponent mixture is stabilized against unwanted contact with moisture. The dryers are preferably used in predetermined quantities and are homogeneously incorporated in active form in the multicomponent mixture. Their quantity and capacity determine
30 the time beyond which moisture penetrating by diffusion is no longer bound by the dryer and leads to hydrolysis and hence release of the masked weak carboxylic acid. On the other hand, the presence of typical selected reducing agents provides for stabilization against unwanted contact
35 with oxygen. In this case, too, it is possible through the

particular quantity of reducing agent used to influence the time beyond which the system is activated by oxygen with formation of hydroperoxide. It is clear that, in individual cases, considerable freedom to influence the course of the reaction is obtained through this dual control possibility. Thus, it may be desirable for example to achieve full saturation of an applied paint or adhesive film with oxygen without premature barrier formation occurring through early initiation of polymerization at the surface of the reactive material. It may be desirable in this case to delay the starting reaction by delayed hydrolysis of the masked acid using a relatively large quantity of the drying agent. Conversely, however, the concentration of free acid in the exposed film of material may be increased by initially inhibiting the oxidation reaction through the use of a comparatively larger quantity of reducing agent so that, immediately after the start of the oxidation reaction, a relatively large amount of free acid is available for the reaction.

Various mechanisms are available for inhibiting the "autox" system used in accordance with the invention, of which the five basic types 1 to 5 are listed below:

1. stabilization against O_2 , addition of antioxidants
2. stabilization against H_2O , addition of drying agent
3. stabilization against $R-OOH$, addition of reducing agent
4. stabilization against radicals, addition of radical inhibitors
5. stabilization against premature acid formation (H^+), addition of bases

From general knowledge of chemistry, typical stabilizer components are listed in the following, the numbers in brackets after the particular compound indicating which of the five mechanisms listed above is to be assigned to the stabilizer:

pyrogallol (1), O_2 -inhibited acrylates (1), hydroquinone (1,4), hydroquinone monomethyl ether (1,4), substantially dehydrated zeolites, particularly zeolite A of low water content (2), metal salts binding water of crystallization, 5 for example anhydrous copper sulfate (2), triphenyl phosphine (3), tributyl phosphite (3), butyl hydroxytoluene (4), phenothiazine (4), anhydrous basic oxide compounds, such as Al_2O_3 basic and/or CaO (5), dicyclohexyl carbodiimide (2).

10 In the multicomponent mixtures according to the invention, the activator mixtures preferably make up no more than about 25% by weight and, in particular, no more than about 10% by weight, based on the weight of the system as a whole. Depending on the activity of the components used, 15 the weight of the activator mixture can be greatly reduced, for example to about 0.1% by weight or to at least about 0.5% by weight. Particularly suitable quantities of the activator system are at least about 1% by weight, preferably up to about 8% by weight and more preferably from 20 about 1 to 7% by weight. All these figures are based on the one hand on the total weight of the multicomponent system according to the invention and the total weight of the three principal components of the activator system.

The three principal components of the activator system 25 may advantageously be used in the following quantitative ratios to one another (in % by weight, based on the mixture of the three activator constituents):

5 to 20% and preferably 5 to 15% of the metal compound
30 to 60% and preferably 40 to 55% of the tertiary amine 30 compound
30 to 60% and preferably 40 to 55% of the masked weak acid.

The particular quantities in which the metal compounds are used may also be defined in particular through the ratio by weight of the weight of the metal to the weight of 35 the multicomponent activator system as follows:

Preferred quantities of metal compound are from 0.01 to 5% by weight, preferably from 0.05 to 2% by weight and more preferably from about 0.1 to 1% by weight metal, based on the total weight of the activator constituents.

5 If inhibitors and/or stabilizers of the type mentioned above are used to control the course of the reaction and/or the open pot life, the quantities in which they are used will be gauged according to the stated purpose. In each individual case, they may readily be determined by consid-
10 erations appropriate to the expert and/or by preliminary tests. This is also illustrated purely by way of example in the form of a comparison: where a metal salt forming water of crystallization, for example copper sulfate, is used for the primary binding of moisture penetrating by
15 diffusion, it will have to be used in larger quantities - purely in terms of weight - than in the case where triphenyl phosphine is used in the corresponding inhibition of diffusing oxygen. The regulators used will normally not exceed a few percent, for example about 2 to 5% by weight,
20 of the mixture as a whole and are generally used in quantities of less than 1% by weight.

In another embodiment, the present invention relates to the activator systems - described in detail at the beginning - of the three components tertiary amine com-
25 pound, at least partly soluble metal component and hydrolyzable masked compound of the weak acid with pK_s values of the free acid of no less than about 0.9. All numerical and factual data on the definition of these components also apply in the same way to this embodiment of the invention.

30 The invention also relates to the use of the activator systems for initiating reactions of radically polymerizable systems containing ethylenically unsaturated components by contact with oxygen and water and more especially by contact with ambient air, preferably at room temperature or
35 only slightly elevated temperature. More particularly, the

invention relates in this regard to the use of activator systems in acrylate- and/or methacrylate-based polymerizable materials or mixtures or comparable systems based on compositions containing styrene and/or acrylonitrile, for example mixtures of styrene and unsaturated polyester resins.

In one particularly important embodiment, the invention relates to aerobic adhesive systems which may be present in particular in the form of a one-component adhesive packed in storable form and which are characterized by the use of the activator mixtures according to the invention. In further embodiments, the invention relates to the use of these activator systems for surface coating with polymerizable, in particular spreadable coating materials. In a preferred variant of this embodiment, the invention provides spreadable air-drying paint systems which are preferably solvent-free. Finally, in another embodiment, the invention relates to the use of suitable systems, for example the above-mentioned styrene/unsaturated polyester resin systems, for the production of mouldings with initiation of the reaction involved by contact with ambient air.

Systems of the above-described type frequently contain combinations of low molecular weight, ethylenically unsaturated monomers and preformed oligomers and/or polymers which are compatible with the monomers used and, in particular, are at least partly soluble therein. The content of radically polymerizable components in such multicomponent mixtures, particularly their monomer content, is at least about 20% by weight and preferably at least about 40% by weight. Taking into account the boundary condition of at least slightly elevated viscosity, monomer contents may reach upper limits of 60, 80 or even 90% by weight. More specifically, the general knowledge of the expert applies in this regard. Oligomeric or polymeric components added to the multicomponent mixture may in turn

contain reactive groups, particularly ethylenically unsaturated groups, or may even be free from such groups. Finally, however, it is also known that the need to use low molecular weight monomeric compounds may be virtually eliminated if it is possible to ensure that a mixture consisting solely of preformed oligomeric and/or polymeric compounds at least partly accessible to the radically initiated polymerization or crosslinking reaction can be handled and, in particular, processed by moulding.

10

Examples

Example 1

A mixture of

- 15 44.5% MMA
45 % polyester polyurethane consisting of
2 mol CAPA 200 (a polycaprolactone manufactured by UCC, OH value 209)
3 mol 2,4-tolylene diisocyanate (Desmodur T 100, a product of Bayer AG)
20 1 mol B-Ö1/20 (a polypropylene glycol monobutyl ether manufactured by Hoechst, OH value 75)
1 mol hydroxyethyl methacrylate
5 % tetraacetoxo diboroxane
25 5 % N,N-dimethyl-p-toluidine
0.5% cobalt naphthenate (cobalt content 6%)
cures in air in 60 minutes in a layer thickness of about 1 to 2 mm. By reducing the layer thickness to the usual film thickness for adhesives, the curing time is reduced to 20
30 minutes.

Example 2

The adhesive mixture consists of

- 49.5% by weight MMA
35 40 % by weight soluble filler (Plexigum MB 319, Röhm)

- 5 % by weight tetraacetoxy diboroxane
- 5 % by weight N,N-dimethyl-p-toluidine
- 0.5% by weight cobalt naphthenate.

5 The multicomponent mixture is prepared from anhydrous components and is stored after degassing in an inert gas atmosphere.

10 For bonding, the adhesive mixture is applied to the surfaces to be bonded and exposed to the ambient air for 3 to 5 minutes. After the start of the reaction - as reflected in clouding and incipient skin formation - the substrates are bonded and fixed.

After storage for 24 hours at room temperature, material failure occurs in the tensile shear testing of bonded PVC sheets.

15

Examples 3 to 8

Mixtures of

- 65 % MMA
- 28 % Plexigum MB 319
- 20 3.5 % N,N-dimethyl-p-toluidine
- 3.5 % carboxylic acid derivative
- 0.03% Co(II) acetyl acetonate and optionally
- 0 - 1000 ppm inhibitor

25 cure on contact with ambient air. For bonding, the parts to be bonded are thinly coated, fitted together after 3 to 5 minutes (skin formation) and optionally fixed. Tensile shear strength was determined after 24 hours.

Example No.	Carboxylic acid derivative	Pot life (mins)	Tensile shear strength (PVC) (N/mm ²)
5			
3	Tetraacetoxy diboroxane	60	7.9 (MF)
4	Tetraacetoxy diboroxane	60	6.5 (MF)
10	addition of 200 ppm tri-phenyl phosphine		
5	Acetic acid trimethyl silyl ester	150	3.0 (MF)
6	Propionic acid trimethyl silyl ester	180	1
15			
7	Tetraacetoxy silane	15	10.5 (MF)
8	Trimethyl silyl methacrylate	64	1.5

20 MF = material failure

Example 9

A mixture of

62 %	tetrahydrofurfuryl methacrylate
31 %	Plexigum MB 319
0.03%	Co-acetyl acetate
3.5 %	N,N-dimethyl-p-toluidine
3.5 %	tetraacetoxy diboroxane

has a pot life of 60 minutes on contact with ambient air.

30 Bonding carried out in accordance with Examples 4 to 9 produced tensile shear strengths of 7.5 N/mm² on PVC and 7.6 N/mm² on iron.

Example 10

35 A mixture of

63 %	MMA
27 %	Plexigum MB 319
3 %	Mn(II) octoate
3.5 %	N,N-dimethyl-p-toluidine

3.5 % tetraacetoxy diboroxane
polymerizes 15 minutes after contact with the atmosphere.

Example 11

5 An activator system of 5% by weight dimethyl-p-toluidine, 5% by weight tetraacetoxy diboroxane and 0.5% by weight cobalt naphthenate solution is added in a quantity of 89.5% by weight to the commercial product "Diacryl 101" (dimethacrylate of bisphenol A x 2 EO) in the absence of
10 further reactive monomer components.

After exposure of this mixture to air, the material polymerizes in one hour (surface tackiness) and cures in one day.

Similar behaviour is observed where cyclohexyl meth-
15 acrylate is used.

**CLAIMS**

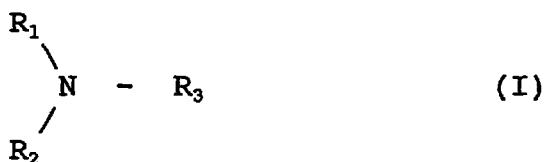
1. Mouldable, radically polymerizable multicomponent mixtures containing
 - ethylenically unsaturated, polymerizable compounds, if
5 desired in admixture with soluble and/or insoluble fillers and/or other auxiliaries
 - an activator system initiatable by contact with oxygen,
characterized in that these multicomponent mixtures contain
10 an activator system based on the following principal components which can be initiated by contact with oxygen and water and, in particular, by contact with ambient air:
 - N-alkyl-substituted tert.arylamines containing at
least one aliphatic CH bond in the α -position
 - 15 - metal compounds at least partly soluble in the system to accelerate the drying of unsaturated oils and
 - compounds of weakly acidic carboxylic acids having pK_a values of no less than about 0.9 which can be hydrolyzed to the free carboxylic acid on contact with
20 moisture.
2. Multicomponent mixtures as claimed in claim 1, characterized in that they are formulated as a one-component system non-reactive in the absence of air or even as a multicomponent system non-reactive on contact with air, the
25 multicomponent systems being in particular two-component systems in which the tert. N compound is kept separate from the metal compounds and the compounds hydrolyzable to free carboxylic acids.
3. Multicomponent mixtures as claimed in claims 1 and 2,
30 characterized in that they are free - particularly when formulated as a non-reactive one-component system - from reactive groups, particularly reactive hydrogen atoms, for example in the form of OH and/or -COOH groups which lead to premature release of the weakly acidic carboxylic acids.
- 35 4. Multicomponent mixtures as claimed in claims 1 to 3,



characterized in that they are formulated as a system designed for activation on contact with ambient air at ambient temperature or only slightly elevated temperatures.

5. Multicomponent mixtures as claimed in claims 1 to 4, characterized in that they are formulated as a free-flowing and preferably slightly thickened spreadable to paste-like material.

6. Multicomponent mixtures as claimed in claims 1 to 5, characterized in that they contain as N-alkyl-substituted arylamines compounds corresponding to general formula I



in which

R_1 is an optionally substituted aryl radical, more especially an optionally alkyl-substituted phenyl radical,

R_2 has the same meaning as R_1 or is an optionally substituted, linear or branched alkyl radical and

R_3 is a linear or branched alkyl radical which may even be substituted, but has at least one H atom in the α -position to the N.

7. Multicomponent mixtures as claimed in claims 1 to 6, characterized in that dialkyl aniline compounds substituted or unsubstituted in the ring, of which the alkyl radicals each preferably contain up to 10 and more preferably up to 6 C atoms, are present as compounds corresponding to general formula I, aniline derivatives optionally alkyl-substituted in the ring, especially those of the structure of dimethyl aniline and/or dimethyl-p-toluidine, being particularly suitable.



8. Multicomponent mixtures as claimed in claims 1 to 7, characterized in that they contain compounds of metals occurring in several valency stages, more especially compounds of corresponding transition metals, the metal ions preferably being present in their low valency stage, as the metal-containing driers at leastly partly soluble in the system.
9. Multicomponent mixtures as claimed in claims 1 to 8, characterized in that they contain metal compounds - soluble in organic media - of cobalt and/or manganese or even iron, the iron even being useable in the form of an Fe^{3+} compound.
10. Multicomponent mixtures as claimed in claims 1 to 9, characterized in that they contain compounds of carboxylic acids having pK_s values no lower than about 1 and preferably no lower than about 1.3 which hydrolyze on contact with moisture.
11. Multicomponent mixtures as claimed in claims 1 to 10, characterized in that they contain masked, moisture-hydrolyzable compounds having an upper pK_s limit of approximately 13 and preferably of approximately 11.5 and, more particularly, corresponding carboxylic acid compounds in which the free carboxylic acid has an upper pK_s limit of about 7.
12. Multicomponent mixtures as claimed in claims 1 to 11, characterized in that they contain masked carboxylic acids containing one or more carboxyl groups and, more particularly, 1 to 4 carboxyl groups.
13. Multicomponent mixtures as claimed in claims 1 to 12, characterized in that they contain the weak carboxylic acids in the form of their anhydrides and/or as mixed anhydrides with other weak carboxylic acids and/or as mixed anhydrides or esters with hydroxy compounds of hetero atoms, more particularly corresponding compounds of boron and/or silicon.
14. Multicomponent mixtures as claimed in claims 1 to 13,



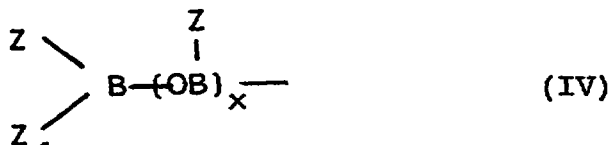
characterized in that they contain hydrolysis-labile derivatives of weakly acidic carboxylic acids corresponding to general formula II



5 in which

R_4 is an optionally substituted alkyl, cycloalkyl or aryl radical and X is a weakly acidic, substantially neutral or, in the extreme case, very weakly basic radical which can be eliminated by hydrolysis at at most slightly elevated temperatures with simultaneous formation of the free acid R_4COOH .

10 15. Multicomponent mixtures as claimed in claims 1 to 14, characterized in that they contain hydrolysis-labile derivatives of general formula II in which X represents a radical corresponding to the general formula IV



20

in which the Z's may be the same or different and have the following meanings:

25 a radical $R_5-CO-O-$, where R_5 is the same as or different from the radical R_4 in general formula II and, in particular, represents alkyl, cycloalkyl or aryl radicals which in turn may be substituted with the proviso that the free carboxylic acid R_5COOH formed during hydrolysis at least corresponds to the lower limit mentioned for the pK_s value

30

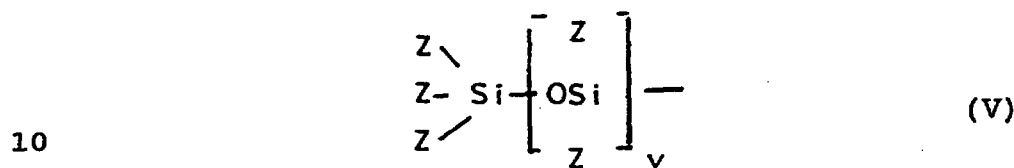
and/or Z represents alkyl, cycloalkyl and/or aryl radicals which in turn may optionally be substituted and/or attached to the boron by an oxygen atom,

35

x has a value of 0 to 2, more especially 1.



16. Multicomponent mixtures as claimed in claims 1 to 13, characterized in that they contain compounds of general formula II in which X is a radical corresponding to general
5 formula V



in which

Z has the meaning defined in reference to the compounds of general formula IV and y has a value of 0 to about 10 and, more particularly, a value of about 5.

- 15 17. Multicomponent mixtures as claimed in claims 1 to 16, characterized in that they contain as ethylenically unsaturated polymerizable components acrylate and/or methacrylate compounds or systems, styrene or styrene derivatives and/or acrylonitrile which may even be completely or partly
20 present in the form of reactive preformed oligomer and/or polymer compounds.

18. Multicomponent mixtures as claimed in claims 1 to 17, characterized in that they additionally contain fillers, thickeners, elasticizing agents, pigments, coupling agents
25 and stabilizers which are soluble and/or insoluble in the system.

19. Active-substance mixtures as claimed in claims 1 to 18, characterized in that they contain dryers in active form for stabilization against unwanted contact with
30 moisture and/or reducing agents for stabilization against unwanted contact with oxygen

20. Multicomponent mixtures as claimed in claims 1 to 19, characterized in that the activator mixture makes up no more than about 25% by weight and preferably no more than
35 10% by weight of the system as a whole and preferably makes up at least 0.1% by weight and, more preferably, about 1 to



8% by weight of the system as a whole.

21. Multicomponent mixtures as claimed in claims 1 to 20, characterized in that the components of the activator system are used in substantially the following quantitative ratios to one another (in % by weight, based on the mixture of the three constituents of the activator):

5 to 20 and preferably 5 to 15% metal compound or

0.01 to 5 and preferably 0.05 to 2% by weight metal

30 to 60 and preferably 40 to 55% tert. amine compound

10 30 to 60 and preferably 40 to 55% of the masked weak acid.

22. Multicomponent mixtures as claimed in claims 1 to 21, characterized in that their content of radically polymerizable components, particularly their monomer content, is at least about 20% by weight and preferably at least about 40% by weight.

23. Multicomponent mixtures as claimed in claims 1 to 22, characterized in that, in their in-use form, they have a minimum viscosity of about 30 mPas, preferably of at least about 100 mPas and, more preferably, of at least about 300 mPas (Brookfield).

24. The use of the multicomponent mixtures as claimed in claims 1 to 23 as an aerobic adhesive system, particularly in the form of a one-component adhesive packed in storable form.

25 25. The use of the active-substance mixtures claimed in claims 1 to 23 for surface coating, more particularly as a spreadable, air drying paint system and for the production of plastics mouldings.