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[54] ACTIVATED NICKEL CATALYSTS 12 Claims, No Drawings

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ABSTRACT: Nickel-containing foraminous material is formed by leaching about 2–100 percent by weight of the aluminum from an alloy consisting essentially of about 25–47 percent by weight of nickel and about 53–75 percent by weight of aluminum, at least about 65 percent by weight of the nickel in the alloy being present as intermetallic NiAl_3 compound. This foraminous material is useful as an activated catalyst for the hydrogenation of organic compounds and as an anode in fuel cells.

ACTIVATED NICKEL CATALYSTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to improved nickel-containing foraminous materials and to their use as activated nickel hydrogenation catalysts and as anodes in fuel cells.

2. Description of the Prior Art

Conventional Raney nickel catalysts are prepared by melting mixtures containing 35–60 percent by weight of nickel and 40–65 percent by weight of aluminum to form melt solutions. The exothermic heat of reaction between the nickel and aluminum raises the temperature to about 1,400° C. The molten mass is then rapidly cold cast into iron molds. When the molten mass has cooled, the ingot is mechanically reduced to particles of the desired size. These particles are then activated by treatment with an aqueous alkali solution which leaches aluminum from the alloy thereby leaving a foraminous material having active nickel at the surface. These materials are widely used as catalysts in hydrogenation reactions in the chemical industry.

SUMMARY OF THE INVENTION

It has now been discovered that nickel-containing foraminous materials having improved activity as hydrogenation catalysts can be formed by leaching about 2–100 percent by weight of the aluminum from an alloy consisting essentially of about 25–47 percent by weight of nickel and about 53–75 percent by weight of aluminum, at least about 65 percent by weight of the nickel in the alloy being present as intermetallic NiAl_3 compound.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered in accordance with this invention that the activity of activated nickel hydrogenation catalysts depends, among other things, upon the percentage of the nickel in the original nickel-aluminum alloy present as intermetallic NiAl_3 compound. The terms "intermetallic NiAl_3 compound" and " NiAl_3 phase," as used throughout the specification and claims are intended to refer to the composition of the crystalline grains of pure NiAl_3 unit crystals in the microstructure of the alloy.

It has been found in conjunction with this invention that, in the case of conventional Raney nickel alloys, including alloys of 42 percent by weight nickel and 58 percent by weight aluminum, which are nominally NiAl_3 , less than about 60 percent by weight of the nickel in the alloy is present as intermetallic NiAl_3 compound. It has been found that a large proportion of the nickel in these alloys is present as the intermetallic compounds, Ni_2Al_3 and NiAl .

Although it is not intended that this invention be limited to any particular theory, it is believed that the most active catalysts are those formed from alloys containing the highest proportion of nickel in the NiAl_3 phase. This theory is based on the belief that the most active nickel sites are those which result when aluminum is leached from the NiAl_3 phase. The activated catalysts of this invention, which are derived from alloys having from about 65 percent to greater than about 80 percent of their nickel content in the NiAl_3 phase, are generally about 1.5 to 3 times as active as conventional activated Raney nickel catalysts in the hydrogenation of benzene.

The percentages of nickel in the NiAl_3 phase recited throughout the specification and claims were determined by conventional analytical procedures. A polished surface of the alloy is examined under a microscope to determine the percentage of the major phase present, and the composition of the major phase is determined by conventional X-ray analytical techniques as described in "X-ray Diffraction Procedures," by H. P. Klug and L. E. Alexander, published by John Wiley and Sons, New York, 1954.

The alloys which are useful in preparing the foraminous materials of this invention consist essentially of about 25–47

percent by weight of nickel and about 53–75 percent by weight of aluminum, and have at least about 65 percent by weight of the nickel present as NiAl_3 phase. The term "consisting essentially of," as used throughout the specification and claims, is meant to include unspecified ingredients or impurities in the alloy which do not materially affect the basic and novel characteristics of the catalyst. That is, this term excludes only unspecified ingredients or impurities in amounts which prevent the advantages of this invention from being realized.

The optimum alloy for use in accordance with this invention contains about 58 percent by weight of aluminum and about 42 percent by weight of nickel which is the weight ratio of these ingredients in the intermetallic compound NiAl_3 . When the amount of nickel present exceeds about 42 percent, however, there is a tendency to form increasing amounts of Ni_2Al_3 and NiAl phases. Accordingly, the alloy preferably consists essentially of about 35–45 percent nickel and about 55–65 percent aluminum and most preferably about 38–42 percent nickel and about 58–62 percent aluminum. When the alloy contains less than about 35 percent by weight of nickel, it can still contain a quite high proportion of the nickel in the NiAl_3 phase since the excess aluminum tends to be present as metallic aluminum. Such catalysts, however, are less economical than those derived from the preferred nickel-aluminum alloy since the aluminum removed from the metallic aluminum phase during the activation step does not result in the formation of active nickel sites.

The alloy may be prepared by any process which results in at least about 65 percent by weight of the nickel being present as the NiAl_3 phase. Preferably at least about 70 percent by weight of the nickel in the alloy is in the NiAl_3 phase, and most preferably at least about 75 percent by weight. Alloys have been prepared in which at least about 80 percent by weight of the nickel is in the NiAl_3 phase.

A preferred process which is commercially suitable for preparing the alloys used to prepare the foraminous materials of this invention comprises reacting a mixture consisting essentially of about 25–47 percent by weight of nickel and about 53–75 percent by weight of aluminum at a temperature above about 825° C. sufficient to form a single-phase homogeneous melt, cooling the resulting mass to a temperature below about 854° C., annealing the resulting mass at about 790°–854° C. for at least about 30 minutes until at least about 65 percent by weight of the nickel in the alloy is in the NiAl_3 phase, and allowing the resulting mass to cool to atmospheric temperature. The term "annealing" is used herein to describe the heat treatment used to develop an equilibrium amount of solid NiAl_3 phase mixed with the liquid phase.

The manner in which the nickel and aluminum are mixed together and heated is not critical provided a single-phase homogeneous melt is formed. Generally a temperature of at least about 825° C. is necessary, and preferably a temperature of at least about 900° C. is reached. When metallic aluminum and metallic nickel are mixed at these temperatures, an exothermic reaction takes place which raises the temperature to about 1,400° C.

The manner in which the molten mass of nickel and aluminum is handled after it is formed is of critical importance to the formation of a maximum amount of NiAl_3 phase. If the molten mass is quenched below its crystallization temperature by normal procedures, such as cold casting, less than about 60 percent of the nickel will be in the NiAl_3 phase. In order to obtain alloy containing at least about 65 percent by weight of the nickel in the NiAl_3 phase, it is necessary to anneal the liquid-solid mixture at temperatures of about 790°–854° C. for at least about 30 minutes. The time required for the annealing step will depend upon the particular temperature used. At temperatures of about 800° C. it may be necessary to heat for about 4 hours. At temperatures of about 850° C. annealing times as short as about 30 minutes may be sufficient. Preferably the annealing is at temperatures of about 840°–854° C. for about 45 to about 75 minutes.

The thermal history of the composition between the initial formation of the homogeneous melt and the annealing step is not important. The molten mass can be cold cast to the solid state before the annealing step or it can be cooled to the annealing temperature and held at that temperature during the annealing step. In any event, the annealing step increases the NiAl_3 phase content of the resulting alloy. After the annealing step the resulting mass is allowed to cool to atmospheric temperature in any convenient manner. The term "atmospheric temperature," as used herein, is intended to include outside and room temperature.

The resulting alloy is then subjected to mechanical reduction in particle size to a suitable size for catalytic material such as about 0.5 micron to about 3 centimeters in diameter. The particular particle size will depend upon whether the catalyst is to be used as a slurried catalyst or a fixed-bed catalyst. When used as a slurried catalyst, the particle size is preferably about 325–200 mesh. When the catalyst is used in a fixed bed, the particle size is preferably about 20 mesh to about 2.5 centimeters in diameter.

The alloy used in accordance with this invention is activated by contacting it with an aqueous alkali metal hydroxide solution until about 2–100 percent by weight of the aluminum is leached from the alloy. When the activated catalyst is used in a slurry system, generally about 85–100 percent of the aluminum is leached from the alloy. When the catalyst is used in a fixed bed, generally about 2–50 percent of the aluminum is leached out and the residual aluminum acts as a support for the nickel. Suitable alkali metal hydroxides include sodium, potassium, lithium, cesium and rubidium hydroxides. The aqueous solution may contain the hydroxide alone or it may also contain buffer components such as alkali metal carbonates. Generally the alkali metal hydroxide solution will contain about 0.1–5 percent by weight of alkali metal hydroxide, and preferably it contains about 0.25–1 percent by weight of hydroxide.

The preferred method of activating the catalyst is to treat the alloy with an aqueous alkali metal hydroxide solution which is fed at a temperature not in excess of about 35°C ., whereby less than about 1.5 moles of hydrogen are evolved for each mole of sodium hydroxide. Preferably the aqueous solution contains about 0.25–1 percent by weight of sodium hydroxide, the exit temperature of the solution during activation does not exceed about 35°C ., and about 2–30 percent by weight of the aluminum originally contained in the alloy is leached out. The term "activated" as used herein is intended to refer to both the original activation of the fresh alloy and to the reactivation of the same alloy after it has lost its activity through use.

The nickel-containing foraminous materials of this invention are suitable for use in all applications which have heretofore been found to be useful for Raney nickel-type catalysts. They are particularly useful as catalysts for the hydrogenation of organic compounds to compounds of increased hydrogen content. Suitable reactions include the hydrogenation of carbon-carbon double and triple bonds such as the conversion of aryl, alkenes and alkynes to the corresponding more saturated or completely saturated compounds. Suitable reactions include the conversion of benzene to cyclohexane, cyclododecatriene to cyclododecane, butadiene to butene or butane and butynediol to butanediol. Other hydrogenation reactions include the conversion of nitro compounds to amines. The hydrogenation of cyano compounds to amines such as the hydrogenation of adiponitrile to hexamethylene diamine, the hydrogenation of esters to alcohols, the hydrogenation of ketones to secondary alcohols, the hydrogenation of aldehydes to alcohols, the hydrogenation of alkyl anthraquinones to alkyl anthrahydroquinones, and the complete hydrogenation of any of the above compounds to hydrocarbons.

Use of the activated catalysts of this invention leads to a number of process advantages in hydrogenation reactions. Substitution of the catalyst of this invention for a conventional

Raney nickel catalyst in many cases allows the reaction to be completed in considerably less time than was previously required. On the other hand, it may be desirable to increase the concentration of the feed material or decrease the size of the catalyst bed rather than shortening the reaction time. Another advantage of the catalyst of this invention is that it tends to initiate hydrogenation reactions at a lower feed temperature.

In hydrogenation reactions using a conventional Raney nickel fixed-bed catalyst the useful life of the catalyst can be increased by substituting an activated catalyst of this invention for the conventional catalyst and removing only one-half as much aluminum during activation of the improved catalyst as was removed from the conventional catalyst. Such a catalyst will have approximately the same activity as the conventional catalyst but will undergo twice as many reactivations.

The activated catalysts of this invention are particularly suitable for the hydrogenation of cyclododecatriene to cyclododecane. This reaction is normally carried out using a conventional Raney nickel-type fixed-bed catalyst of about 2–10 mesh size from which about 15–25 percent by weight of the aluminum has been removed. The feed mixture containing about 5–15 percent by weight of cyclododecatriene and about 85–95 percent by weight of cyclododecane is passed over the catalyst at a temperature of about $125^\circ\text{--}250^\circ\text{C}$. and a pressure of about 25–30 atmospheres at the rate of about 0.25–0.4 part by weight of feed mixture per part of catalyst per hour.

When using the improved catalyst of this invention in the hydrogenation of cyclododecatriene, the amount of aluminum leached out during the initial activation could be reduced to about 5–15 percent with the result that a second activation of the catalyst could be carried out after the catalyst becomes spent. On the other hand if about 15–25 percent of the aluminum is leached from the improved catalyst of this invention, the concentration of cyclododecatriene in the feed mixture could be increased to about 10–20 percent by weight or the weight ratio of feed mixture per hour to catalyst could be increased to about 0.6–0.75. The temperature at which the reaction is initiated could also be reduced to about 100°C . when using the more active catalyst of this invention.

The improved catalysts of this invention are also particularly useful for the conversion of 2-butyne-1,4-diol to 1,4-butanediol. The reaction is normally carried out with a conventional fixed-bed Raney nickel-type catalyst of 2–10 mesh size which has been activated by removal of about 15–25 percent of the aluminum. The reaction is carried out using an aqueous feed containing about 20–70 percent butynediol and about 30–80 percent water, a hydrogen partial pressure of about 150–400 atmospheres, and a superficial gas velocity of at least about 0.5 foot per minute at a temperature of about $60^\circ\text{--}150^\circ\text{C}$. and a recycle to fresh feed ratio of about 10–40:1.

In the hydrogenation of butynediol using the improved catalyst of this invention, removal of only about 2–5 percent of the aluminum during activation would provide a suitable catalyst which could be reactivated in situ. Using an improved catalyst of this invention having about 15–25 percent of the aluminum removed could allow a decrease in the size of the catalyst bed, an increase in the rate at which the butynediol is fed to the reactor, or an increase in the total quantity of butynediol which can be converted before the catalyst becomes spent thereby increasing the effective life of the catalyst.

The improved catalysts of this invention are also useful for the hydrogenation of alkyl anthraquinones to alkyl anthrahydroquinones. This hydrogenation reaction is generally used as one step in a cyclic process for making hydrogen peroxide. In this process an alkylated anthraquinone is hydrogenated to the corresponding alkylated hydroanthraquinone in a slurry of hydrogenation catalyst. The catalyst is filtered out and the resulting medium is contacted with air to form hydrogen peroxide and alkylated anthraquinone. The hydrogen peroxide is recovered and the alkylated anthraquinone is reconverted to alkylated hydroanthraquin-

one in the hydrogenation step. In the hydrogenation step of such a process the activated catalyst of this invention could be slurried with a solution containing alkylated anthraquinone, alkylated hydroanthraquinone and a suitable solvent. Suitable alkylated anthraquinones include 2-ethylanthraquinone, 2-tert.-butylanthraquinone, 2-amyl-anthraquinone, tetrahydro derivatives of the above anthraquinones, and mixtures thereof. The reaction takes place at about 25°–50° C. while charging hydrogen at atmospheric or slightly elevated pressure.

The nickel-containing foraminous materials of this invention can also be used as the anode in fuel cells such as hydrogen-oxygen fuel cells. In preparing the anode nickel-aluminum alloy powder is mixed with water and pressed into the shape of the anode. The alloy powder is then sintered and activated with dilute aqueous alkali metal hydroxide solution to leach aluminum from the surface of the anode. The anode is then placed in a fuel cell, for example a hydrogen-oxygen fuel cell, containing a conventional cathode such as a silver electrode and operated at about 92° C. with about 35–38 percent by weight aqueous potassium hydroxide as the electrolyte. The oxygen and hydrogen are supplied at about 25 p.s.i.g.

EXAMPLES OF THE INVENTION

The following examples, illustrating the preparation and use of the foraminous materials of this invention, are given without any intention that the invention be limited thereto. All parts and percentages are by weight.

EXAMPLE 1

An alloy containing 28 percent nickel and 72 percent aluminum was melted at 1,100° C. The melted mass was allowed to cool fast to form an ingot. The ingot was melted at 975° C., the melt was lowered through the furnace and a rectangular ingot in the shape of a bar was withdrawn from the furnace at the rate of 3.4 millimeters per hour with the point of solidification being maintained just below 854° C. The ingot was then cooled to atmospheric temperature. Examination of the interior of the ingot indicated a major portion of intermetallic NiAl_3 compound.

The alloy was powdered by filing with an iron file to particles of 50–100 mesh size. The powdered alloy was slurried in an aqueous solution of one normal sodium hydroxide at 15° C. The rate of addition of powdered alloy to the solution was sufficiently slow that the temperature did not reach 35° C. The temperature was also controlled by having the reaction vessel partially immersed in an ice bath. The quantity of alloy particles added to the caustic solution was limited so that only 50 percent of the sodium hydroxide was utilized in the activation. After the evolution of hydrogen subsided, the temperature of the contents of the vessel was gradually raised to the boiling point and held there for 10 minutes. The medium was then cooled and the activated catalyst was repeatedly water washed with decantation until the sodium ion was completely removed as indicated by the absence of sodium ion in the wash water. The catalyst was then washed repeatedly with methanol by decantation until about 98 percent of the water was removed. The catalyst was then repeatedly washed with cyclohexane until about 99 percent of the methanol was removed and the catalyst was stored as a slurry in cyclohexane. Spectrographic analysis of the catalyst for impurities indicated the presence of 0.2–0.3 percent of cobalt as the only detectable impurity.

The activity of the catalyst was determined by the hydrogenation of benzene at 120°–150° C. About 250 parts of a mixture of 10 percent benzene and 90 percent cyclohexane were mixed with 1 part of the above catalyst in a closed vessel and hydrogen was supplied at a pressure of 2,000 p.s.i. The benzene was completely converted to cyclohexane after 6.25 minutes.

EXAMPLE 2

A mixture containing 42 percent nickel and 58 percent aluminum was heated to 1,120° C. in an inert atmosphere at which temperature it became fluid. The material was then transferred to another furnace at 837° C., after which the temperature in the furnace was slowly decreased to 800° C., over a 30-minute period and maintained at 795° C. for an additional hour. The heat was then turned off and the material was allowed to cool to atmospheric temperature in the closed furnace over a 16-hour period. Metallographic investigation of the ingot showed a coarse cellular structure having intermetallic NiAl_3 compound as the major phase and Ni_2Al_3 phase present in some of the cells. The interstices between the cells contained aluminum.

The above alloy was reduced in particle size and activated as described in example 1. The activated catalyst was then used in the hydrogenation of benzene to cyclohexane as described in example 1. The reaction time for 100 percent conversion of benzene to cyclohexane was 10.25 minutes.

EXAMPLE 3

A mixture of 42 percent nickel and 58 percent aluminum was slowly heated to 1,216° C. in an alumina crucible which had been previously baked at 250° C. under vacuum for 16 hours to remove water. Melting was done in a melt chamber using induction heating and an inert atmosphere. After melting was completed, the temperature was maintained between 1,216° C. and 1,204° C. for 11 minutes. The molten material was hot cast into a crucible steel mold preheated at 700° C. and allowed to cool from 854° C. to 800° C. in a furnace over a period of 70 minutes. The ingot was then allowed to cool in the furnace to room temperature. X-ray powder diffraction and metallography investigation of the resulting ingot revealed that the sample consisted of about 80 percent NiAl_3 phase, about 10 percent Ni_2Al_3 phase, and only a trace of aluminum.

The alloy was reduced in particle size and activated as described in example 1. The activated catalyst was then used in the hydrogenation of benzene to cyclohexane by the procedure of example 1. The time for 100 percent conversion of benzene to cyclohexane was 9 minutes.

EXAMPLE 4

An alloy was prepared from a mixture containing 36 percent nickel and 64 percent aluminum following the procedure of example 3, except that the melt chamber was heated slowly to 1,033° C. at which point the temperature rose sharply to 1,160° C. in 5 minutes. The material was cast into slab molds and allowed to cool from 850° C. to 800° C. over a period of 30 minutes. X-ray diffraction analysis indicated that the sample contained NiAl_3 , Ni_2Al_3 and Al phases. Metallographic investigation showed a dendritic core of Ni_2Al_3 surrounded by NiAl_3 with aluminum filling the interdendritic spaces. The NiAl_3 phase content was about 70 percent.

The alloy was reduced in particle size and activated as described in example 1. The activated catalyst was then used to hydrogenate benzene to cyclohexane as described in example 1. The time for 100 percent conversion of benzene to cyclohexane was 13 minutes.

EXAMPLE 5

A commercially obtained Raney nickel alloy containing 42 percent nickel and 58 percent aluminum was annealed by heating at 800° C. for 4 hours. The resulting material was allowed to cool in the furnace as in example 3. The resulting alloy was reduced in particle size and activated as described in example 1. The resulting activated catalyst was used in the hydrogenation of benzene to cyclohexane as in example 1. The time to 100 percent conversion of benzene to cyclohexane was 14.5 minutes.

For comparison, a conventional Raney nickel catalyst was prepared by melting a mixture of 42 percent nickel and 58

percent aluminum under exothermic conditions. The molten mass was then cold cast into iron molds. After the molten mass had cooled the ingot was mechanically reduced to particles of 50-100 mesh and activated as described in example 1. This standard Raney nickel catalyst was then used in the hydrogenation of benzene to cyclohexane as described in example 1. The reaction time for 100 percent conversion of benzene to cyclohexane was 20 minutes. This conventional Raney nickel catalyst was arbitrarily assigned a relative reaction rate of 100. The relative reaction rates of the improved catalysts of the examples were determined by comparing the reaction time to 100 percent conversion using the conventional catalyst to the reaction time to 100 percent conversion using the improved catalyst in accordance with the equation:

$$\text{Rate imp. cat.} = \frac{\text{Rate conv. cat.} \times \text{Time conv. cat.}}{\text{Time imp. cat.}}$$

The following table shows the time to 100 percent conversion of benzene to cyclohexane for the improved catalysts of the examples. The relative reaction rates based on the conversion times are also given.

Example	Time to 100% Conversion, minutes	Relative Reaction Rate
1	6.25	325
2	10.25	195
3	9	220
4	13	155
5	14.5	140
Conventional Cat.	20	100

Although the invention has been described and exemplified by way of specific embodiments, it is not intended that it be limited thereto. As will be apparent to those skilled in the art, numerous modifications and variations of these embodiments can be made without departing from the spirit of the invention or the scope of the following claims.

I claim:

1. A nickel-containing foraminous material formed by leaching 2-100 percent by weight of the aluminum from an alloy consisting essentially of 25-47 percent by weight of nickel and 53-75 percent by weight of aluminum, at least 65 percent by weight of the nickel in the alloy being present as intermetallic NiAl_3 compound.

2. The foraminous material of claim 1 in which 5-100 percent by weight of the aluminum is leached from the alloy, the alloy consists essentially of 35-45 percent by weight of nickel and 55-65 percent by weight of aluminum, and at least 70 percent by weight of the nickel in the alloy is present as intermetallic NiAl_3 compound.

3. The foraminous material of claim 2 in which the alloy consists essentially of 38-42 percent by weight of nickel and 58-62 percent by weight of aluminum, and at least 75 percent by weight of the nickel in the alloy is present as intermetallic NiAl_3 compound.

4. The foraminous material of claim 3 in which at least 80 percent by weight of the nickel in the alloy is present as intermetallic NiAl_3 compound.

5. The foraminous material of claim 3 in which 85-100 percent by weight of the aluminum is leached from the alloy and the material has a particle size of 325-200 mesh.

6. The foraminous material of claim 3 in which 2-50 percent by weight of the aluminum is leached from the alloy and the material has a particle size of 20 mesh to 2.5 centimeters in diameter.

7. The method of hydrogenating cyclododecatriene to cyclododecane which comprises passing a feed mixture containing 5 to 20 percent by weight of cyclododecatriene and 80 to 95 percent by weight of cyclododecane with hydrogen over a nickel-containing foraminous catalyst material in accordance with claim 1 at the rate of 0.25 to 0.75 part by weight of feed mixture per part of catalyst per hour, at a temperature of 100° to 250° C. and a hydrogen pressure of 25 to 30 atmospheres.

8. The method of claim 7 in which the catalyst is in a fixed bed, is 2 to 10 mesh in size, and has had 5 to 25 percent by weight of the aluminum removed from the original alloy.

9. The method of hydrogenating 2-butyne-1,4-diol to 1,4-butanediol which comprises passing an aqueous feed containing, by weight, 20 to 70 percent butynediol and 30 to 80 percent water with hydrogen over a nickel-containing foraminous catalyst material in accordance with claim 1 at a hydrogen partial pressure of 150 to 400 atmospheres, a superficial gas velocity of at least 0.5 foot per minute at a temperature of 60° to 150° C. and a recycle to fresh feed ratio of 10:1 to 40:1.

10. The method of claim 9 in which the catalyst is in a fixed bed, is of 2 to 10 mesh in size, and has had 2 to 25 percent by weight of the aluminum removed from the original alloy.

11. The method of hydrogenating alkyl anthraquinone to alkyl anthrahydroquinone which comprises reacting a solvent slurry containing alkylated anthraquinone, alkylated hydroanthraquinone and a nickel-containing foraminous catalyst material in accordance with claim 1 with hydrogen at atmospheric to slightly elevated pressure and at a temperature of 25° to 50° C.

12. The method of claim 11 in which the alkylated anthraquinone is selected from the group consisting of 2-ethylanthraquinone, 2-tert.-butylanthraquinone, 2-amylanthraquinone, tetrahydro derivatives thereof, and mixtures thereof.

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