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(54) Title: MOLASSES BIO BINDER PRODUCTION AND APPLICATIONS THEREOF

(57) Abstract: The invention is related to a molasses binder production method used to produce isolation materials utilized in the entire furniture industry, such as wood panels (chipboard, MDF, plywood), and in the recent years rock wool, basalt wool and fibreglass, which can be substituted with formaldehyde based binders.



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MOLASSES BIOBINDER PRODUCTION AND APPLICATIONS THEREOF**5 Technical Field**

The invention is related to a molasses binder production method used for producing isolation materials that are utilized in the entire furniture industry, such as wood panels (chipboard, MDF, plywood), and in the recent years, rock wool, basalt wool and fibreglass, that can be substituted with formaldehyde based binders.

Known State of the Art (Prior Art)

Particularly there are four basic formaldehyde based thermosetting resins used commonly, in the woodworking industry. These are,

-phenol formaldehyde

-resorcinol formaldehyde

-urea formaldehyde

-melamine formaldehyde.

Phenol formaldehyde resins are resins that are obtained as a reaction of the condensation of phenol and formaldehyde. They are durable against water, organic solvents and fungi and pests. This resin is mostly preferred in the production of wood products that are to be used outdoors as they exhibit high durability against environmental air conditions. At the same time, nowadays, this resin is being used in the production of basalt wool.

Resorcinol formaldehyde resins, are resins which are quite durable against water and are also the most expensive resins. Due to this reason, they are produced in small amounts and are preferred especially when water resistance is necessary.

Urea formaldehyde resins are the most commonly used resins, as they are cheap. They are used in the production of wooden plates such as chipboards, MDF, plywood and werzalit. The hardening time in hot pressing is shorter and the colour is transparent. Its resistance against water is quite low in comparison to phenol based resins.

Melamine formaldehyde resins, are quite expensive even though they have higher resistance against water in comparison to urea formaldehyde resins. For this reason it is used together with urea formaldehyde or only for surface coating purposes. Besides being expensive the most important disadvantage of this resin is that its storage life is short. Due to this, production is carried out and stored in solid form and it is wetted at the area of usage.

In short, all four of these resins that have been mentioned are produced as a result of condensation reaction with formaldehyde. They release formaldehyde to the medium after disintegration due to environmental conditions both during the production of these resins and after these resins are brought to their final state. This condition which is called formaldehyde emission, cannot be completely eliminated even if the products that participate in the disintegration during storage or during a mid stage are reduced and even if complete condensations reactions are provided by controlling the production conditions of resin. Formaldehyde emission changes depending on F/U (formaldehyde/urea) mol ratio in particularly urea formaldehyde resins. When F/U mol ratio is high, the durability of the product increases and at the same time formaldehyde emission also increases. When F/U mol ratio decreases, the strength of the product decreases and this also reduces formaldehyde emission. For this reason, manufacturers are in search of a product which shall reduce formaldehyde emission without affecting the quality of the final product. Various chemicals are added into the resin as formaldehyde scavengers and formaldehyde emission is reduced. However these additional chemicals that are used as formaldehyde scavengers are expensive and therefore they are not used extensively. Studies for producing novel resins that are affordable and that do not contain formaldehyde are being continued.

Formaldehyde is produced by catalytic oxidation of methanol and it is the smallest member of aldehydes. It is a colourless, strong odored, viscous and toxic fluid which is weak in acidity and which can be mixed with water. The negative effects on formaldehyde against human

health are known and in 2004, the Cancer Research Agency which is an affiliate of the World Health Organization has classified formaldehyde as a substance which causes cancer in humans. Due to this reason the formaldehyde emission limit values, standards and test methods have been determined in relation to products that are produced with formaldehyde based resins. The formaldehyde emission limit value in wood based plates and the test methods thereof, which are accepted in Europe have been given in Table 1. The formaldehyde test methods and limit values used for particle board and MDF in our country has been provided in Table 2.

10 **Table 1. European formaldehyde standards**

Board type	Test method	Limit values
Particle Board (PB),MDF	EN 120:1992 Perforator Method	≤8 mg/100 g E1 >8 mg/100 g E2 ≤30 mg/100 g E2
All wood panels	EN 717-1:2004 Room method	≤0,124 mg/m ³ E1 >0,124 mg/m ³ E2
All wood panels	EN 717-2:1994 Gas Analysis Method	≤3,5 mg/m ² .h

Table 2. Formaldehyde standard test methods and limit values for Particle Board and MDF.

Class	Test Method	Limit values
E1 Class	Perforator (EN120)	Content ≤8 mg/100 oven dried board mass
	Wood based boards- determination of formaldehyde release- Section 1: Emission of formaldehyde by room method (EN 717-1)	Release ≤0,124 mg/m ³ air
E2 Class	Perforator (EN120)	Content >8 mg/100 g oven dried board mass Content ≤20 mg/100 g oven dried board mass
	Wood based boards- determination of formaldehyde release- Section 1: Emission of formaldehyde by room method (EN 717-1)	Release >0,124 mg/m ³ air and ≤0,3 mg/m ³ air

15 It is known that during the production of resins which contain formaldehyde, during the preparation of products using resins, and the usage of the end products obtained with such resins in homes and workplaces release formaldehyde that causes cancer, continuously to the environment. Nearly all furniture, kitchen cabinets, tables, doors are produced using urea

formaldehyde, melamine formaldehyde and mixtures thereof. Similarly, in order to provide heat insulation, houses and workplaces are cladded with rockwool, basalt wool or glass fibre. In the production of these products, besides formaldehyde which is hazardous to human health, more harmful phenol formaldehyde resins that comprise phenol are also used. As a result of the usage of these products that contain formaldehyde based resins, people continue to inhale this formaldehyde all the time, which is cancerous. As a result we can observe that cancer cases have been increasing very rapidly.

Due to this reason the aim of the invention is to produce a high quality, affordable organic resin which does not comprise phenol and formaldehyde and which is not harmful to human health. This resin that is to be produced, must be able to be used instead of phenol formaldehyde in production and instead of the rockwool, basalt wool used for insulation and melamine formaldehyde used in coating and urea formaldehyde used as a binder in the wood working industry and it should improve the characteristics of the end product instead of compromising the characteristics thereof. For example, as the products such as chipboards, MDF, werzalit, and plywood that are to be obtained with the resin that is to be produced according to the invention shall be much more resilient than those produced with urea formaldehyde resin, the product may not necessitate coating with papers impregnated with melamine formaldehyde [1-4].

Several studies are being carried out in this field as it has been noticed that, it is crucially important in terms of human health for such non-cancerous resins not containing formaldehyde and phenol to be produced and used. However any kind of study similar to ours, in literature which shows that these materials are used in the production of isolation materials such as rockwool, basalt wool, and glass fibre and wood products such as chipboard, MDF, plywood and werzalit, as binders [5-7] that are molasses-based and water insoluble, that are obtained by adding ammonium nitrate, sulphuric acid and phosphoric acid to molasses used in the production of bricks that can be used for insulation, from pumice and in the production of metallurgical coke, production of coal, coke powder and anthracite, has not been found.

The main aim of our invention, is to determine if these molasses based resins that we have previously produced can be used for this aim or not. It has been determined that the resins

produced, as a result of our studies that have been ongoing for many years, can be used instead of the formaldehyde based resins and industrial scaled applications have been carried out in a werzalit factory. The studies that have been carried out and the results obtained have been described in detail below.

5

After the negative effects of formaldehyde on human health has been realized, several studies have been carried out to produce binders that do not contain formaldehyde. Some of these studies have been mentioned below:

- 10 According to the study carried out by Li Kaichang numbered US 20080213597, a hardener and a binder which do not contain soy protein and/or lignite and formaldehyde are prepared. The hardener is selected from two different groups of compounds. The first group of compounds that can be used as a hardener is one of a heterocyclic functional group compound comprising amine, amide, imine, imide and nitrogen, boron compounds, IA group
15 oxide and hydroxides, IIA group oxide and hydroxides. The second group of compounds that can be used as a hardener can be selected from a reaction product of ethylenediamine and epichlorohydrine reaction product, a reaction product of bis-hexamethylenetriamine and epichlorohydrine or reaction products of hexamethylenediamine and epichlorohydrine.
- 20 In the study carried out by Mingfu Zang et al., numbered US 8,809,477 at least three compounds that can constitute a covalent bond with each other are prepared. One of these three compounds is selected from protein and the other two are selected from cross linking compounds. The protein can be selected from vegetable or from animal proteins such as soy protein, maize protein, keratin, gelatine, casein, gluten and albumin. One of the compounds
25 used as a cross linkers a homopolymer and/or copolymer which is one of the polycarboxy polymers that comprises carboxyl. The homopolymer and/or copolymer of carboxylic acid such as acrylic acid which comprises ethylenic non saturated carboxylic acid, metacrylic acid, methyl maleic acid and itaconic acid can be used. The second cross linking compound which is to be used must comprise at least two functional groups and must be able to easily react
30 with both the protein and the other polymer based cross linking compound. Poliols, alkanolamines, polyamines can be used for this.

In the study carried out by Bernd Reck et al., numbered US 6,099,773 a binder is produced

from the reaction of alkanolamine comprising at least two hydroxyl groups and the polymer produced with the free radical polymerization of an ethylenic unsaturated acid anhydride or an ethylenic unsaturated dicarboxyl acid.

- 5 The binder that has been prepared can harden in 15 minutes at 130°C following a drying process for 72 hours at 50°C. Compounds that comprise phosphor are used as reaction catalysts of the polymer and alkanolamine used.

10 In the study carried out by Christopher M. Hawkins et al., numbered US 20110021101, an aqueous binder is prepared by means of a binding agent such as starch and a silane derivative. At the same time, it comprises a binder citric acid, polyacrylic acid, a cross linker such as triethanol amine, polyamine, glycerine, a catalyst such as sodium hipophosphate, sodium phosphate and potassium tripolyphosphate. A silane derivative can be used from the compounds of aminosilane, epoxy trialkoxysilane, methacryl trialkoxysilane, methacryl
15 nitrohydroxy silane as a binding agent.

In the study carried out by Somaieh Salehpour et al., numbered WO 2016/101063, starch is used as biopolymer together with isocyanides. It is defined that the mass ratio of biopolymer and isocyanides used, can be within the range of 15:85-50:50 and that urea needs to be
20 present in the aqueous binder that has been prepared.

In the study carried out by Liang Chen et al., numbered WO 2004/050978, a binder without formaldehyde is produced by adding polycarboxylic acid to the product that has been obtained after polyacid monomer and polioliol are mixed until a reaction is formed. All of the
25 monomer or oligomers that comprise at least two carboxylic acid groups having a molecular weight between 50-1000 can be used as a polyacid. Maleic acid, maleic anhydrite, fumaric acid, citric acid, adipic acid, tartaric acid, itoconic acid and compounds thereof can be used as a polyacid monomer. Compounds such as, glycerine, glucose, sorbitol, triethanolamine, monoethanolamine, diethanolamine comprising at least two hydroxyl groups that can form
30 an ester bond with polyacids can be used as polioliol.

In the study carried out by Thor Husemoen et al., numbered US20030153690, a suitable resin is obtained for mineral wool products (glass fibre, basalt wool, rockwool) following the

mixing of carboxylic acid and an alkanolamine under reaction conditions. The obtained resin is reacted with a polymer that comprises a carboxylic acid and its features are being tried to be enhanced. A carboxylic acid such as an adipic acid, citric acid, succinic acid comprising more than two carboxyl groups can be used as carboxylic acid and a compound such as diethanolamine, triethanolamine, n-butyl-diethanolamine, can be used as alkanolamine. A polymer such as polyacrylic acid, polymethacrylic acid, poly-maleic acid having a molecular weight between 1000-250000 is used as polymer.

In the study carried out by Erling Lennart Hansen et al., numbered EP1382642, following the reaction of at least an alkanolamine and at least a carboxylic acid a product is obtained and this product is reacted with a carbohydrate and as a result an aqueous binder without formaldehyde suitable for mineral fiber is obtained. A carboxylic acid anhydride such as succinic anhydride, maleic anhydride, and phthalic anhydride is used as a carboxylic acid anhydride, an alkanolamine such as diethanolamine, diisopropanolamine, methyl-diethanolamine, and triethanolamine can be used as alkanolamine, and a carbohydrate such as glucose, fructose, starch, pectin, and xylose can be used as a carbohydrate.

All of the binders that have been briefly described above, are binders that do not comprise formaldehyde. However some of these binders that have been prepared are either very expensive or some of the chemical agents used in the preparation of these binders are cancerous substances that are much more dangerous than of formaldehyde.

Besides these, studies related to the production of binders that have been prepared by using molasses that are by products of sugar factories that can be easily and economically obtained, are also present.

According to the study carried out by Tsuyoshi Tamogami et al., numbered WO2017/104134, it has been disclosed that a binder produced by mixing the ammonium salts of the strong acid of molasses with salts such as magnesium chloride, sodium chloride can be used in the production of chipboard and MDF.

Brief Description of the Invention and its Aims

A study which discloses a binder prepared from molasses using strong acid in order to produce a wooden panel (werzalit, chipboard, MDF, plywood) and rockwool, glass fibre, basalt wool has not been encountered. On the other hand the binder production method from molasses without formaldehyde using strong acids and/or ammonium nitrate at the ratio of 2,5-5% only, that we have developed in this study, is cheaper and a more suitable binding production method in comparison to the binder studies without formaldehyde that have been mentioned in literature.

Detailed Description of the Invention

The resins subject to our invention can be used in all fields where formaldehyde based binders that lead to cancer in humans, and it does not have any harmful effects on people. At the same time, as our invention has continuous raw material resources, it is a very cheap resin production method and application in comparison to urea formaldehyde and phenol formaldehyde.

Empirical Studies

The raw materials of the resins that have been prepared are molasses, sulphuric acid, phosphoric acid and ammonium nitrate. Molasses have been obtained from sugar factories and its approximate characteristics have been provided in table 3. Ammonium nitrate is ammonium nitrate that is used as fertilizer comprising 33% nitrogen.

Table 3. General characteristics of Molasses

Characteristics	Percent Composition (%)
Dry matter	77,3
Crude ash	8,5
Crude protein	7,1
Organic substances	68,8
Substances without nitrogen	58,7

Preparation of the Resin

When resin is being prepared, the solid matter amount that the resin needs to contain has been calculated depending on usage field. 2,5%-5% of the solid matter in molasses that the resin needs to contain depending on the solid matter amount is a hardener constituting sulphuric acid, phosphoric acid and/or ammonium nitrate, wherein aqueous solutions comprising these hardeners are prepared, molasses is added onto these solutions and is slowly mixed until a homogenous mixture is obtained.

10 Example 1: The resin comprising 64% solid matter that can be replaced with urea formaldehyde in the production of werzalit is prepared as follows: 171,25 g water is acquired. 15,75g acids or ammonium nitrate from the acids that are to be used as hardeners are added in the water. A homogenous mixture is obtained after mixing. Onto this aqueous solution 813 g molasses comprising 77,3% solid matter is added and mixed. Mixing is
15 continued until a homogenous mixture is obtained. The obtained resins are ready to be used.

Example 2: The resin comprising 50% solid matter that can be used instead of urea formaldehyde in the production of chipboard and MDF is prepared as follows: 355,79 g water is acquired. 12,21g ammonium nitrates or acids that are to be used as hardeners are added
20 in the water. A homogenous mixture is obtained after mixing. Onto this aqueous solution 632 g molasses comprising 77,3% solid matter is added and mixed. Mixing is continued until a homogenous mixture is obtained. The obtained resins are ready to be used.

As it can be seen from these two examples, resin is prepared similarly for the production of
25 rockwool, basalt wool, glass fiber and plywood. The solid matter amount is prepared according to processing conditions. For example, after the solid matter is adjusted according to the type of the wood to be used in the production of chipboard the required amount of an adhesive is changed by $\pm 5\%$ and products with the desired features and quality can be obtained.

30

Industrial Application of the Resin

The industrial applications of the binders we have prepared have been carried out in a werzalit factory. Standard production in a werzalit factory is performed as follows: After the received woodchips are dried, it is mixed with urea formaldehyde that is used as an adhesive at a ratio of 25%-30% depending on the type of woodchips, and is then shaped in cold press. Following this, impregnated paper is placed on a plate that has been prepared and the product is placed into a hot press. The final product is obtained after pressing for 5-7 minutes at a temperature of 155-160°C.

10

The industrial application of the resin subject to our patent has been carried out under the standard production conditions of a factory. However in order for the resin to be turned into a plate that can maintain its initial shape in a cold press, calcium oxide and/or magnesium oxide is added to the chipboards following the calcium oxide and/or magnesium oxide adhering process such that they do not exceed 0,5-0,1% of the resin added to the chipboards. By this means, calcium oxide and/or magnesium oxide is reacted with the saccharide in the resin that is molasses based and magnesium-saccharide and/or calcium saccharide is obtained following pre-polymerization reaction and this enables the plate to be taken out of the cold press after it is partially hardened, without losing its form. These plates that are received from the cold press is placed in a hot press, and after being kept under pressure for 5-7 minutes at temperatures above 150°C, the acidic resin is cross linked and the required strength is provided to the final product. The water soluble saccharides that are magnesium-saccharides and/or calcium saccharide obtained partially following the cold press, react with the acid ions available in the medium in order to provide water insoluble salts.

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Production has been carried out using molasses based resin comprising 2,5% phosphoric acid, 2,5% sulphuric acid and 2,5% ammonium nitrate, without changing the production conditions of the factory. The obtained results have been shown in table 4.

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Table 4. Characteristics of the produced Werzalit

Characteristic	Test Standard of the Characteristic	Limit Value	Unit	Product produced with urea formaldehyde	Product produced with 2,5% phosphoric acid resin	Product produced with 2,5% ammonium nitrate resin	Product produced with 2,5% sulphuric acid resin
Formaldehyde emission	TS EN 12460-3 Wood based boards- Determination of formaldehyde release Section 3: Gas analysis method	3,5	mg/m ² -h	8,19	0	0	0
Screw retaining ability	TS EN 320 Particle boards and fiber boards – Determination of Screw retaining ability	10	Kg.f/mm	15,54	25,21	19,09	22,07
Bending strength	TS EN 310 Wood based boards- Determination of bending resilience and bending module	200	Kg.f/cm ²	281,453	380,831	357,051	371,959
Water absorption ability	TS EN 318 Wood based boards- Determination of change in sizes depending on relative humidity changes	2,5	cm	5	2,2	3,8	2,5
Width expansion in cold water	TS EN 317 Particle boards and fiber boards –Determination of width expansion in cold water following immersion in water	5	%	5,7	3,4	6	4
Width expansion in hot water	TS EN 317 Particle boards and fiber boards- Determination of width expansion in cold water following immersion in water	10	%	10,7	4,2	10,2	4,3

When Table 4 is examined, it can be clearly seen that all of the characteristics of the products prepared with molasses resins comprising phosphoric acid and sulphuric acid are above the standard limit values accepted for werzalit. At the same time, the characteristics of the products prepared with these two resins are better than the characteristics prepared with urea formaldehyde. However even though the screw retaining ability and bending strength of the product produced with the molasses resin prepared with ammonium nitrate are higher than standard values, water absorption ability, expansion of width in cold water and expansion of width in hot water are a little above of the standard limits. Moreover the product produced with ammonium nitrate resin changes the colour of the water during water

absorption tests into brown and this shows that the resin cannot become completely insoluble in water. It is understood that the pH value that is required for the ammonium nitrate to be cross linked, cannot be provided.

5 These results clearly show that all of the molasses resins with phosphoric acid, sulphuric acid and ammonium nitrate that we have obtained can be used as binders that do not contain formaldehyde in the production of products such as wood panels (werzalit, chipboard, MDF, plywood etc.) and glass fiber, basalt wool and rock wool. However some changes can be carried out in processing conditions (pressing time, pressing temperature etc.) in order to
10 produce products with desired quality can be obtained following the adjustments of the viscosities and the solid matter amounts of these molasses based resins.

Even though the resins have been prepared with molasses, resins suitable for such aims can be obtained using strong acids and ammonium nitrate from all of the products that contain
15 sugar (white sugar, brown sugar, saccharose, fructose, reduced sugar, glucose syrup etc).

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CLAIMS

1. A wood based panel characterized by comprising sugar based resin as binder.
- 5 2. A wood based panel according to claim 1, characterized by comprising molasses resin as a binder.
3. A wood based panel according to claim 2, characterized by comprising a hardener that is 2,5%-5% by weight of the solid matter that the molasses inside the molasses resin
10 contains.
4. A wood based panel according to claim 3, characterized by the hardener being sulphuric acid, phosphoric acid and/or ammonium nitrate.
- 15 5. A board according to claim 1, wherein said board is chipboard, MDF or plywood.
6. An isolation material, characterized by comprising sugar based resin as binder.
7. An isolation material according to claim 6, characterized by comprising molasses as a
20 binder.
8. An isolation material according to claim 7, characterized in that the molasses resin comprises a hardener that is 2,5% to 5% by weight of the solid matter in the molasses.
- 25 9. A wood based plate according to claim 8, characterized by the hardener being sulphuric acid, phosphoric acid and/or ammonium nitrate.
10. A material according to claim 6, characterized by said isolation material being rockwool, basalt wool and glass fibre.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/TR2019/050647

A. CLASSIFICATION OF SUBJECT MATTER		
B27N 3/00 (2006.01)i; C09J 103/00 (2006.01)i; C09J 105/00 (2006.01)i; C07H 3/02 (2006.01)i; C07H 3/04 (2006.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B27N 3/00; C09J 103/00; C09J 105/00; C07H 3/02; C07H 3/04		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2017104134 A1 (HENKEL AG & CO KGAA [DE]) 22 June 2017 (2017-06-22) Abstract, paragraph 2, 3, 14	1,2,5 3,4
Y	"Molasses and air blown coal tar pitch binders for the production of metallurgical quality formed coke from anthracite fines or coke breeze", Benk A., Coban A., Fuel Processing Technology 92, 2011, 1078-1086.	3,4,8,9
X Y	WO 2011015946 A2 (KNAUF INSULATION [BE]) 10 February 2011 (2011-02-10) Abstract, paragraph 2, 11, 12, claims.	6,7,10 8,9
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Date of the actual completion of the international search 06 January 2020		Date of mailing of the international search report 06 January 2020
Name and mailing address of the ISA/TR Turkish Patent and Trademark Office (Turkpatent) Hipodrom Caddesi No. 13 06560 Yenimahalle Ankara Turkey Telephone No. (90-312) 303 11 82 Facsimile No. +903123031220		Authorized officer Dr. Fadile EZEROĞLU Telephone No. +90 312 303 15 95

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- (1) Claims 1-5
- (2) Claims 6-10

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.