



Synthesis of nitrogen-containing phenolformaldehyde oligomers, grafted with vegetable oils

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Synthesis of nitrogen-containing phenolformaldehyde oligomers (phfo), grafted with vegetable oils is aimed at the acquisition of new range coating materials. Oil has been used as an example of soybean and linseed oils. The interaction between phfo and vegetable oil is carried out by means of functional groups as result of the oxidation processes on carbon atoms adjacent to the double bond and the functional groups, including oligomer macromolecules. Physical-chemical properties of nitrogen-containing as result of modification by means of benzoguanamine (bga) monoalkyl (C_8-C_{12})phfo, grafted with soybean oil is reflected. The probable structure of the nitrogen-containing monoalkyl (C_8-C_{12})phfo, grafted with soybean oil has been studied by means of NMR- and IR-spectroscopy methods. The mechanism of the occurrence of first and second stages of the process are described.

Keywords: nitrogen-containing phenol formaldehyde oligomers; vegetable oils; benzoguanamine; soybean oil; coating materials



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Introduction

Obtaining of coating materials by means of oxidation of vegetable oils and their using as mixture with some resins are known. The solution of the end product of their interaction or their mixture with variety resins in organic solvents (oil paints) are used. Thus, vegetable oils in the main are the ethers of glycerol with unsaturated carboxylic acids, and double bonds play an active role in the oxidation process: the displacement (isomerization) of double bonds, oligomerization of triglycerides, formation of additional functional groups have taken place and they play a positive role in the process of solidification. One of these resins are policondensation product of phenol and its derivatives with formaldehyde.

There are water-soluble coating materials among the phenolic resins [1], grafted with vegetable oils – phenolic oligomers, grafted with soybean oil, which keeps the boron, varnishes and enamels resistant to gasoline – or modified with linseed oil, rosin and only tallowy oil – it is important too [2]. Compounds of this range have been applied as well as high-quality lubricants. Chinese scientists synthesized phfo, modified with linseed oil, which thermal resistance differs from [3-5].

Presented in this article synthesis of nitrogen-containing phfo, grafted with vegetable oils is aimed at the acquisition of new range coating materials. In general, in order to obtain of coating materials the higher the cost of known synthetic resins are to be partially replaced with cheaper vegetable oils. These paints are non-polar solvents (solvent, uayt-spirit) to be the solution, with the superior brightness and high physical-mechanical properties.

Experimental

Oil has been used as an example of soybean and linseed oils. Preference is given to the selection of these oils in their unsaturation. As is well known, the interaction between phfo and vegetable oil is carried out by means of functional groups as result of the oxidation processes on carbon atoms adjacent to the double bond and the functional groups, including oligomer macromolecules, that is why the higher amount of the double bonds has an positive impact on the process. In the following table (Table 1) the composition of used vegetable oils and their physical-chemical parameters, known literature [6] is reflected.

Table 1. Composition and physical-chemical characteristics of vegetable oils

Indicators	Colour	Density, g/sm ³	Freezing temp., °C	n _D ²⁰	Saponification number, mgKOH/100g	Iodine number, mgI ₂ /100g
Butter acids amount, %						
Soybean oil						
Palmitic (C ₁₆) -2,4-6,8	From light to dark yellow	0,928	Negative (8-18)	1,4678	188-195	124-133
Stearic(C ₁₈)-4,4-7,3						
Arachidic(C ₂₀)-0,4-1						
Oleinic(C ₁₈)-32-35,6						
Linoleic(C ₁₈)-51,5-57						
Linolenic(C ₁₈)-2-3						
Linseed oil						
Palmitic (C ₁₆) and stearic(C ₁₈)- 8-10	From yellow to brown colour	0,933	Negative (18-27)	1,4840	191-195	174-183
Oleinic(C ₁₈)- 5-20						
Linoleic(C ₁₈)- 25-50						
Linolenic(C ₁₈)-21-45						

As can be seen from the table, the physical-chemical properties of oils are also close to each other, the composition varies considerably, both amount of unsaturated fatty acids of soybean and linseed oils, as well as the diverse range. These oils have a lower freezing temperature associated with it.



Monoalkyl(C8-C12)phfo of novolac type was synthesized by known method in molar ratio of alkylphenols and formaldehyde 1:0,85, at 98-100°C temperature and acidic medium (pH=3) over a period of 3-4 hours duration. 0,1-0,3 mol bga, bad or kad to 1 mol phenol compound were used as a modifier.

On the second stage the process of interaction between synthesized products and vegetable oil have been studied. For the purpose, oligomers and vegetable oils 1: 3, 1:1, 3:1 ratios by weight of soybean and linseed oil samples were taken. To avoid premature gelatination, part of oligomer (about half) is dissolved in oil sample in 1 hour, the temperature was raised up to 190°C, then add the rest of oligomer mass and was mixed during 3-4 hours at the temperature 230-250°C. The final product is in the form of brown-colored viscous mass. Practices were carried out in air environment, but also to determine the effect of oxidation process in an inert (nitrogen) atmosphere. The material balance data of processes in the first and second phases are presented in Table 2. The final products do not undergo any external change during the period of 5-6 months of storage. They are smooth and homogeneous and mostly in the form of brown-colored mass.

It should be noted that the final product yield is 98-100% taking into account the loss of the process at the level of practice error.

At the initial phase of the study, it was determined, that 1. Oxygen environment is necessary for the interaction of components; 2. Using of the modifiers with nitrogen-containing functional groups has a positive effect to the application of the products.

It should be noted that the natural triglycerides (glycerine esters on base of saturated and unsaturated one-atomic higher fatty acids) makes up ~95-98% of vegetable oils, but the rest of 2-5% consist of free fatty acids (~1-2%), phosphatides – lecithin, kefaline and inosinphosphatides (~0,05-3%), sterin, phytosterins (~0,3-0,5%), pigments and vitamine E (~0,5%) respectively. However, this is a very small amount of impurities, which do not adversely affect performance of the application properties of final product as coating, that is why their separation experiments are not performed and raw vegetable oil is used. According to the choice of vegetable oils, soybean and linseed oils, keeping the more unsaturated acid residue fragments were preferred (these fragments are important to facilitate of hardening and drying of coating materials). But a significant difference in the results of these oils is not observed, that is why for practical work soybean oil was used. As known, the presence of high amounts of linolenic acid residue in composition of coating material leads to get yellow of them over time.

Physical-chemical properties of nitrogen-containing as result of modification by means of bga monoalkyl(C8-C12)phfo, grafted with soybean oil is reflected in Table 3.

As can be seen from the table, the synthesized oligomers unlimited dissolve in the non-polar solvents, such as solvent, uayt-spirit and so on. As known phfo's don't dissolve in non-polar solvents. Moreover, on the second stage at the fixed amount of bga the weight part increase of oligomer from 25% to 75% (example 3-5, 6-8, 9-11) kinematic viscosity acquires high prices and the temperature of softening is determined for the samples richer oligomer.

Table 2. Material balance of synthesis of nitrogen-containing monoalkyl(C₈-C₁₂)phfo, grafted with vegetable oils

№	The composition and quantity of components (%) of oligomers			The composition and quantity of components of oligomers(%), grafted with vegetable oils	
	Monoalkyl-phenols	Formaldehyde	Nitrogen-containing compound	Alkylphfo	Soybean oil
1.	90,1	9,9	-	50	50
2.	90,1	9,9	-	75	25
3.	84,0	9,4	6,6(bga)	25	75
4.	84,0	9,4	6,6(bga)	50	50
5.	84,0	9,4	6,6(bga)	75	25
6.	78,8	8,7	12,5(bga)	25	75
7.	78,8	8,7	12,5(bga)	50	50
8.	78,8	8,7	12,5(bga)	75	25
9.	74,1	8,1	17,8(bga)	25	75
10.	74,1	8,1	17,8(bga)	50	50
11.	74,1	8,1	17,8(bga)	75	25



12.	82,4	9,1	8,5(bad)		50	50
13.	82,4	9,1	8,5(bad)		50	50(linseed oil)
14.	82,4	9,1	8,5(bad)		75	25
15.	76,0	8,4	15,6(kad)		50	50
16.	76,0	8,4	15,6(kad)		75	25

* bga – benzoguanamine, bad – benzamide, kad - karbamide

Table 3. Physical-chemical properties of nitrogen-containing monoalkyl(C₈-C₁₂)phfo, grafted with soybean oil

No	Appearance	Density, kg/m ³	Cryoscopic average molecular weight	Unvolutile compounds, %	Kinematic viscosity (50°C), mm ² /s	Temp. of softening, °C	Solvents
1.	Dark-brown viscous mass	960	1275	97	-	-	All examples are dissolved in benzene, toluene, solvent, uay t-spirit, acetone, DMFA. It is also a good solution. Example 3-5: gasoline, kerosene, diesel fuels – a partial solubility Example 6-8: gasoline, kerosene, diesel fuels – unlimited solubility Example 9-11: gasoline, kerosene, diesel fuels – limited solubility
2.	Dark-brown solid mass	965	-	98	-	-	
3.	Fluid mass, brown, viscous	959	568	95	85,3	-	
4.	Brown viscous mass	976	559	95	569,1	-	
5.	Dark-brown viscous mass	984	526	97	-	43	
6.	Dark-brown transparent viscous mass	978	813	94	466,2	-	
7.	Dark-brown viscous mass	981	687	90	-	-	
8.	Resin-shaped mass of dark-brown	987	1110	96	-	61	
9.	Dark-brown viscous mass	976	567	95	137,0	-	
10.	Resin-shaped mass of dark-brown	976	808	96	-	36	
11.	Resin-shaped mass of dark-brown	990	661	93	-	59	

The judgment compared to a fixed rate of oligomer:oil at the second stage and the molar quantity of nitrogen-containing modifier from 0,1 moles to 0,3 moles (example 3→6→9, 4→7→10, 5→8→11). Thus, viscosity indicators are increased.

The probable structure of the nitrogen-containing monoalkyl(C8-C12)pho, grafted with soybean oil has been studied by means of the NMR- Fourier spectrometer ("Bruker" company, Germany) frequency of 300 MHz. Chemical shifts of atomic groups, related to soybean oil and the initial oligomer have been found in the spectrogram of the final product (Figure 1).

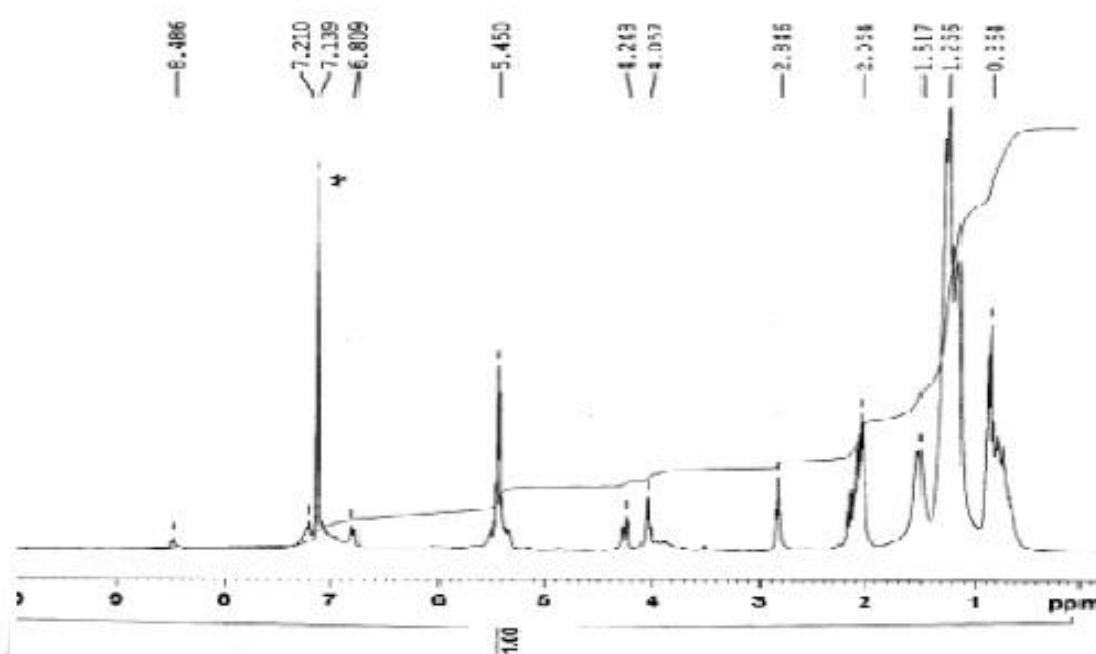


Figure 1. The NMR-spectrogram of the nitrogen-containing monoalkyl(C₈-C₁₂)pho, grafted with soybean oil

For example, the signals in 0.864 ppm are related to the H atoms of CH₃-groups, but in 1,256 and 1,517 ppm -- of -CH₂-groups, respectively. Chemical shifts, related to H atoms of methylene groups (-CH₂-CH=) combined with C atoms forming the double bond, as well as the methylene groups connecting the aromatic nuclear, are observed in 2,054 ppm. H atom signals, corresponding to -CH₂-O-C-CH₂- (2.846 ppm), to -CH₂-O-C-CH₂- (4.057 ppm), to -CH-O-C-CH₂ (4,248-ppm), to -CH=CH- fragments (5,450 ppm) were recorded. The observed chemical shifts in 6,809-7,21 ppm is supposed to be of the H atoms R-OH, Ar-H fragments.

The structure of the nitrogen-containing monoalkyl(C8-C12)phfo, grafted with soybean oil has been studied by means of the IR-Fourier spectrometer ALPHA ("Bruker" company, Germany). Spectral-kinetic investigation was carried out in order to study the mechanism of the process. IR-spectrogram, both the initial components (the nitrogen-containing monoalkyl(C8-C12)phfo, obtained at the first stage and soybean oil), and the sample of the reaction mixture, obtained from their interaction during the interval of ~ 0.5 hours at the second stage, were recorded and compared. The following absorption bands in the spectrogram of initial oligomer are presented: 750 sm⁻¹ - methylene group vibrations, 1370 sm⁻¹ deformation (def.) and 2872 sm⁻¹ valence (val.) C-H bonds of methyl groups, 1456 sm⁻¹ (def.) and 2957 sm⁻¹ (val.) C-H bonds of methylene groups, 1508 sm⁻¹ (def.) and 3027,3060 sm⁻¹ (val.) C-H bonds of the benzene nucleus, 1602 sm⁻¹ (val.) C = C bonds of the benzene nucleus, 783,823,878 sm⁻¹ (def.) C-H bonds of alkyl substitute of benzene nucleus, 1235 sm⁻¹ (def.) and 3307 sm⁻¹ (val.) OH bond vibrations, 1012 sm⁻¹ (def.) O-H bonds of the alcohol groups, 953, 1543 sm⁻¹ (def.) absorption bands corresponding to the NH bond. Except absorption bands in the IR spectrogram of the mixture of nitrogen-containing monoalkyl(C8-C12)phfo with soybean oil (reaction started), valent vibration of C = O bond of ester fragments - 1743 sm⁻¹, as well as absorption bands corresponding to the C = C bonds, which are characteristic for alkene fragments of esters in accordance with the intensity 1651 and 3008 sm⁻¹ are observed in spectrogram of the final product (figure 2).

Presented below in table 4 and 5, the optical density change of the main functional groups in dependence on the duration of the reaction were expressed: C = O (1720,1743 sm⁻¹), C = C (1651,3008 sm⁻¹), the phenol OH (1235 sm⁻¹), NH (1543 sm⁻¹) and the alcohol, in other words, the metilol group -CH₂OH fragments (1012 sm⁻¹). For comparison, the soybean oil (Table 4) and the initial nitrogen-containing monoalkyl(C8-C12)phfo (Table 5) were taken.

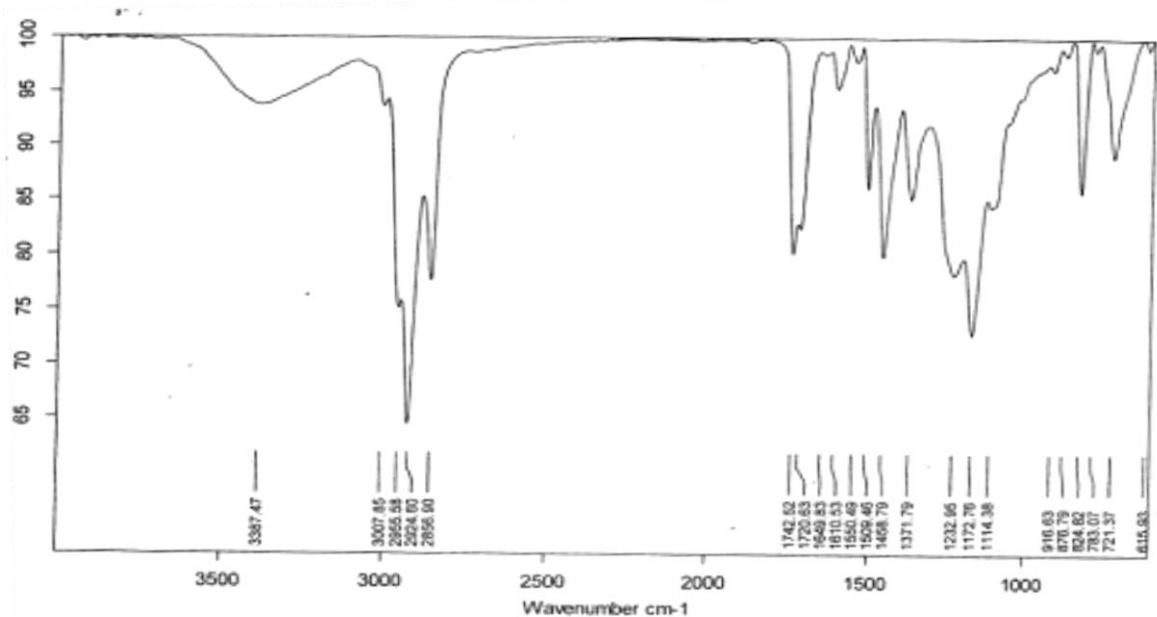


Figure 2. The IR-spectrogram of of the nitrogen-containing monoalkyl(C₈-C₁₂)phfo, grafted with soybean oil

Table 4. The kinetic dependence of optical densities of functional groups on the duration of the reaction

Example	D _{1743 sm⁻¹} (C=O)	D _{1720 sm⁻¹} (C=O)	D _{1743 sm⁻¹} (C=C)	D _{3008 sm⁻¹} (C=C)
Soybean oil	0,272	-	0,007	0,034
Initial mixture	0,107	-	0,006	0,028
After 0,5 hour	0,102	0,082	0,004	0,028
After 1,0 hour	0,099	0,082	0,006	0,028
After 1,5 hour	0,099	0,083	0,006	0,028
After 2,0 hour	0,101	0,084	0,006	0,028
After 2,5 hour	0,101	0,084	0,006	0,028
After 3,0 hour	0,101	0,084	0,006	0,027

Table 5. The kinetic dependence of optical densities of functional groups on the duration of the reaction

Example	D _{1235sm⁻¹} (OH ph.)	D _{1543 sm⁻¹} (N-H)	D _{1012 sm⁻¹} (CH ₂ OH)
Alkylphenol oligomer	0,187	0,047	0,074
Initial mixture	0,108	0,015	0,062
After 0,5 hour	0,107	0,015	0,051
After 1,0 hour	0,106	0,014	0,042
After 1,5 hour	0,106	0,014	0,034
After 2,0 hour	0,107	0,014	0,023
After 2,5 hour	0,106	0,014	0,017
After 3,0 hour	0,105	0,014	0,017

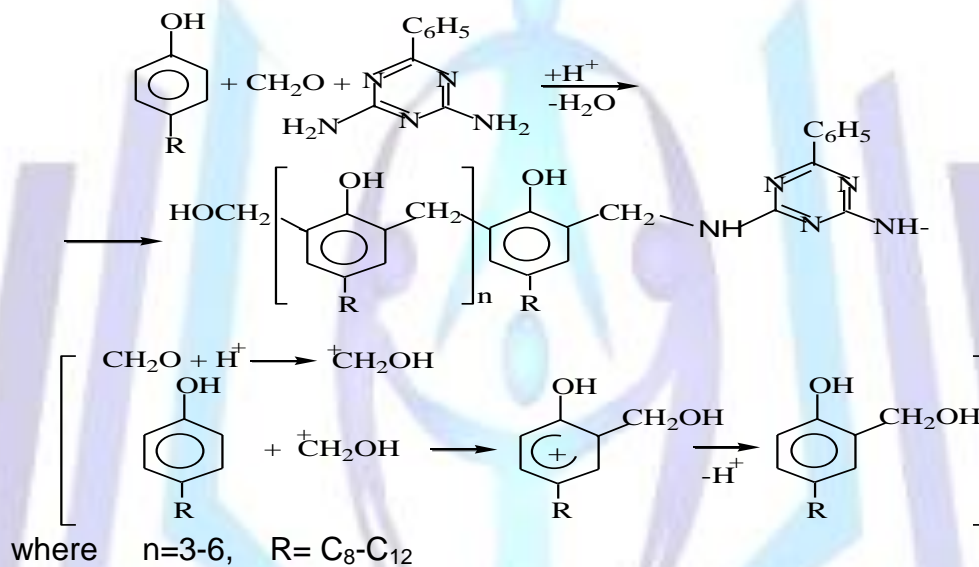


As can be seen from table 4, 1) that the absorption bands indicating the intensity of double bonds in soybean oil are almost unchanged over time, it confirms that the double bonds not spent during the process; 2) carbonyl groups, which included the ester fragments had not been spent, but the new carbonyl groups, which amount ~ is close to amount of these fragments (1720 sm-1) were found. Thus, during the high-temperature oxidation of triglycerides in soybean oil, the formation of new carbonyl group fragments is observed. The optical density of these groups, formed at the first hour of the process is almost constant and remains unchanged up to the end; 3) from the Table 5 is clearly visible that the optical density of the phenolic OH functional groups and the NH fragments is not change over time; 4) the observed ~ 4-fold decrease in the indices of optical density of methylol -CH₂OH groups (at 1012 sm-1) indicates that these groups have been used in the process.

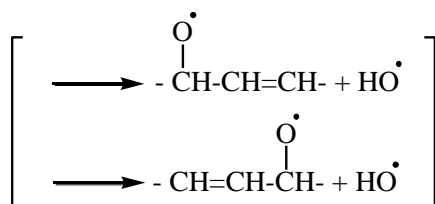
RESULTS

Taking into account the change in the amount of functional groups of soybean oil fragments and oligomer makromolekules, interaction is completed within ~ 2 hours, as well as allows to say that there is no need to spend superfluous time and energy. Analyzes of the results at the second stage indicates that an interaction has happened between themethylol groups of oligomer makromolekules and new functional groups (-OH,-OOH, etc.) of triglyceride fragments of the soybean oil, arising from the oxidation. Taking into account all these, the mechanism of the occurrence of first and second stages of the process are as follows:

I. Synthesis of initial oligomers.



II. 1. Possible reactions of the oxidation process of triglycerides.





The hydroperoxide is not stable and decomposes on heating – homoliz on -O-O- bond occurs and the sources for the extension of the chain have been formed.

The latter radical might be subjected to changes in the following.

The reactions are a portion of processes occurring during the oxidation of triglycerides and confirm the forming of new functional groups of the soybean oil at high-temperature (carbonyl group and OH group, which was supposed to have been spent).

2. The alleged structure of grafted oligomer is as follows.

where $n=3-6$, R- C₈-C₁₂; R₁,R₂-unsaturated acid residue fragments

It should be noted that the molecular weight parameters values allows one to go to the judge [7] about partial destruction processes. Thus, the formation of the small molecular weight fractions on the process of grafting of soybean oil or inessential increasing of molecular weight indicators of high fractions in spite of possibility confirm this assumption.

Synthesised products are recommended as coating materials.

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