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# Methanol Effect on color stability and shelf life of phenolic Resin compound under acidic conditions

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## Abstract

*The object of this work is to investigate the effect of the addition of methanol on the shelf life and color characteristics of novolak resin. Different percentages were added and two mechanisms were suggested for the addition. High ortho structure (1, 2-3) novolak resin was prepared and used in the above investigation. Experimental determination using FT-IR and UV-spectroscopy showed that on the addition of 30% of methanol and according to the second mechanism of addition novolak shelf life increased to 12 months without obvious decomposition and color change. It is suggested that methanol plays an important role in the inhabitation of the reactive sites on the resin that are responsible for the oxidation of the polymer when exposed to atmospheric or storage conditions.*

## Introduction

Phenol, formaldehyde resin is considered to be one of the most important polymers in the molding industry. The first commercially available resin is indeed phenol formaldehyde resin developed by Leo M. Backland in 1907 based on earlier discovery by A. Von Bayer in 1872. Phenolic resins (high ortho figure (1)) are produced by the reaction of formaldehyde with excess phenol under acidic condition (pH = 1 to 3) with typical formaldehyde to phenol ratios are between 0.8 and 0.85. The most common industrial catalysts are oxalic, hydrochloric, sulfuric, phosphoric, and sulfuric acids.

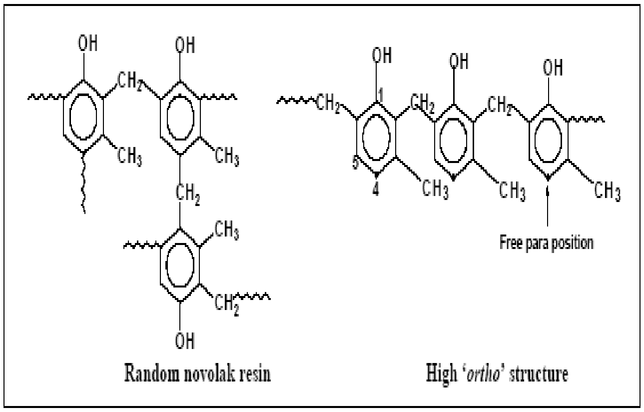
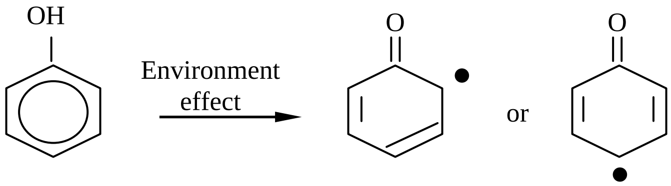


Fig. 1 Random and High ortho novolak structures

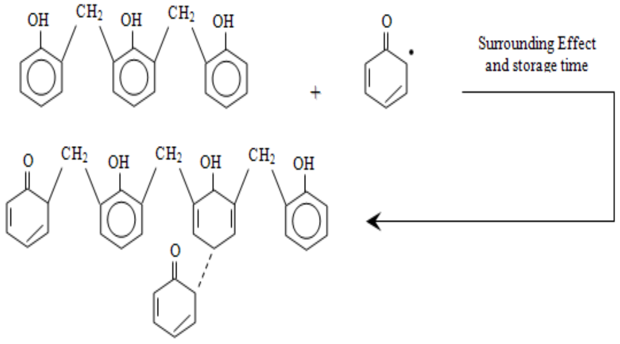
**Color change**

Before(20) use this resin in molding to produce any composite material some properties were changed during storage starting from oxidation to color instability which affect the final composite properties



The main reason for color change of novolak is the existence of un-reacted phenol that is not removed completely from final product that undergoes decomposition reaction (20, 21, and 22). This compound is considered responsible for the color change from colorless to reddish. The above compound known as Quinones root (1, 5, and 22), attacks the polymer chain and causes decomposition by breaking the polymeric chain at these sites.

The following mechanism of attack is proposed:



It is also possible that uneven distribution of reactive site on the polymer may lead to oxidation and consequent decomposition of the final polymer structure.

**Modified resins**

Polymers are considered to be photo-resistant and stable, if they resist the influence of oxidation in an inert atmosphere without changing in their properties significantly.

The following methods are suitable to improve the oxidative resistance of phenolic resins [1]

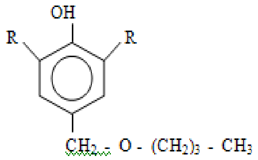
1. Etherification or Estrification of phenolic hydroxyl group.
2. Complex formation with polyvalent elements (Ca, Mg,Zn,Cd,…).
3. Replacement of the methylene linking group by heteroatoms (O,S,N,Si,…).

The most important general modification reactions in phenolic polymer chemistry are the etherification and C-alkylation (Friedel-Crafts) reaction (1). Both reactions are commonly used to enhance flexibility and compatibility with polymers and solvent to reactivity and performance.

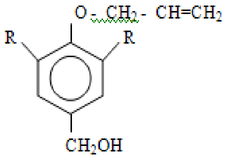
**Etherification reaction**

The hydroxymethyl group in phenol prepolymers can easily be etherified (A) with alcohol because of their tendency to form hydroxybenzylcarbonium ions. High hudroxymethylated phenols and an excess of alcohol are used to avoid the self-condensation reaction. In general the reaction is performed with monoalcohols like methanol, butanol and isobutanol.

On the other hand, the etherification of the phenolic hydroxyl group (O-alkylation (B)) leads to improved alkali resistance. Better flexibility, light fastness and with allyl compounds, enhanced air drying properties are also obtained.



**A**



**B**

*R= H, $CH_2OH$, $CH_2X$*

## Experimental Work

The reaction of phenol with formaldehyde in acid medium proceeds as follows:

$$2C_6H_5OH + CH_2O \rightarrow C_6H_4OHCH_2C_6H_4OH + H_2O$$

Novolak was prepared by reacting formaldehyde with excess phenol under acidic conditions; hydrochloric acid was used as a catalyst. The reaction was carried out in stainless steel batch reactor as shown in figure (2).

High ortho novolak resin was prepared using the following well known ratios (2, 3):-

F/P = 0.8, A/P = 0.01 and W/F = 2.57

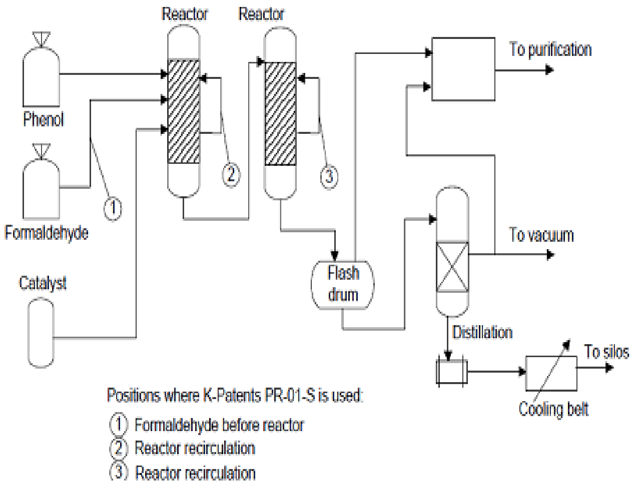


Fig. 2 Equipments used in the production of novolak resin

The reaction was carried out for about 4 hours at an operating temperature of 80oC and pH of 1.5 in a 3 liter stainless steel jacketed reactor. A provision was made for mechanical stirrers to be immersed into the reactor. Other previous were made for a condenser, reactant input, and temperature and pressure control instrument. Products are withdrawn from the bottom of the reactor. Different percentages of methanol added and two mechanisms were suggested for the addition .Methanol ratio was added according to formaldehyde concentration.

**First Mechanism of Addition**

Reactants were added to the reactor according to the molar ratio mentioned earlier (2, 3) and then methanol (20% of the total amount of reactants at 20oC) was added to the reactants at a mixing speed of 500 rpm then, the temperature was raised up to 80oC gradually. Reaction was continued for about 4 hours and novolak resin was formed. Heating was halted and two layers were observed. i.e. water at the top of the novolak was formed. In order to get rid of the water formed as a by-product, the reactor was heated up to 120oC for 2 hours with mixing under 0.1 bar vacuum. To remove about 90% of the formed water.

**Second Mechanism of Addition**

The same procedure above was carried out; however, methanol was added after completion of polymerization i.e. when the two layers of by-product and novolak were formed. Then the mixing and vacuum process was continued until about 90% of the residual water was removed.

The same procedure was carried out several times using different percentage of methanol in order to determine the optimum value. The following ratios were suggested (15, 30, 45 and 60%) based on total volume.

Electronic spectrophotometer measurements were conducted by Schimadzu UV-214 A (UV-Visible Spectrophotometer) using MEK (Methyl Ethyl Keton) as a solvent and a quartz cell of 1.0 cm path length. Samples for that purpose were prepared as shown in table (1).

A comparison was made between samples with methanol added against this with no methanol added using FT-IR.

Table (1): Design parameter for the experimental work

| Run No. | Mixture volume ml. | Methanol volume ml. | Total volume ml. | Percentage of Methanol % |
|---|---|---|---|---|
| 1 | 60 | 0 | 60 | 0% |
| 2 | 60 | 10.6 | 70.6 | 15% |
| 3 | 60 | 25.7 | 85.7 | 30% |
| 4 | 60 | 49 | 109 | 45% |
| 5 | 60 | 90 | 150 | 60% |

## Results and Discussion

Samples were left for a period of about 12 month under ordinary storage at atmospheric conditions and monthly tests were carried out using UV-Spectroscopy and finally FT-IR instruments. Color change was observed by naked eye. The following results are obtained and showed in the table (2).

Short shelf life and color change were observed for samples that were not treated with methanol. A decomposition of its structure is expected due to activity of reactive sites. Methanol was suggested as an additive for two main reasons.

1. Its structural composition is similar to that of formaldehyde.
2. Cheap and readily available.

According to the experimental results the second mechanism of addition was in favor of the first i.e. addition of methanol is suggested to be added after the polymerization step of water mixing and vacuum application for water withdrawal. It could be seen that sample (3) at 30% methanol did not suffer structural and no color change, as shown in table (2) and figure (3).

**First month:**

All samples absorbed the light at (λ = 343 nm) with no color change as shown in data table (2).

**Second to 12th month:**

First sample changed into reddish brown color with (λ = 363 nm ±5) as shown in table (2).

**Third to 12th month:**

All samples showed decomposition and color change except sample (3) with 30% methanol addition as shown in table (2). The value of λ was 345 nm ±2 during the above periods.

The effect of methanol addition on the polymer can be explained as follows:

Assists in the withdrawal of by-product water formed in reaction which considered being a physical process (16, 17, 18, and 22).

Inhibit reactive sites of –CH2 groups i.e. that exist on the high ortho novolak which is considered to be a chemical process (11, 16, 17, and 19).

The effect of methanol addition on the un-reacted chemical can be explained as follows:

1. Complete the phenol – formaldehyde reaction and obtain further novolak which is a chemical process (11, 19, and 20).
2. Get ride of un-reacted phenol from reaction mixture which is considered responsible for the decomposition of novolak structure during storage and hence reducing the shelf life (10, 11, 12, and 15).

FT-IR test made for samples (1) and (3) indicated the fact that methanol addition according to the second mechanism was of physical meaning and was not chemically oriented since no structural changes were observed as shown in figures (4, 5 and 6).

Fig.3 The change in color for sample (1) and (3) after 12 month of novolak resin

Table (2): UV-visible results for each sample with the methanol percentage deferent during 12 month

| Samples | month period | Methanol % | λ | Color change |
|---|---|---|---|---|
| 1 | 1 | 0 | 343 | No change |
| 2 | 1 | 15 | 343 | No change |
| 3 | 1 | 30 | 343 | No change |
| 4 | 1 | 45 | 343 | No change |
| 5 | 1 | 60 | 343 | No change |
| Samples | month period | Methanol % | λ | Color change |
| 1 | 2 | 0 | 343 | change |
| 2 | 2 | 15 | 343 | No change |
| 3 | 2 | 30 | 343 | No change |
| 4 | 2 | 45 | 343 | No change |
| 5 | 2 | 60 | 343 | No change |
| Samples | month period | Methanol % | λ | Color change |
| 1 | 3 | 0 | 343 | change |
| 2 | 3 | 15 | 343 | change |
| 3 | 3 | 30 | 343 | No change |
| 4 | 3 | 45 | 343 | change |
| 5 | 3 | 60 | 343 | change |
| Samples | month period | Methanol % | λ | Color change |
| 1 | 12 | 0 | 343 | Strong change |
| 2 | 12 | 15 | 343 | Strong change |
| 3 | 12 | 30 | 343 | No change |
| 4 | 12 | 45 | 343 | Strong change |
| 5 | 12 | 60 | 343 | Strong change |

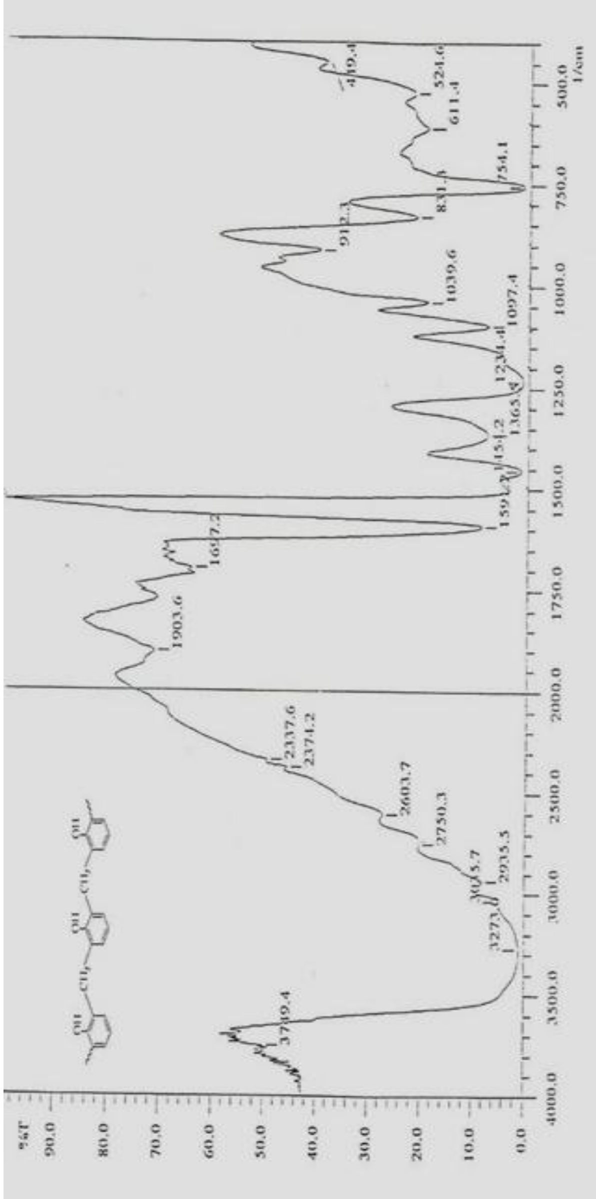


Fig.4FT-IR Standard Plot of Ortho Novolak Resin without Decomposition

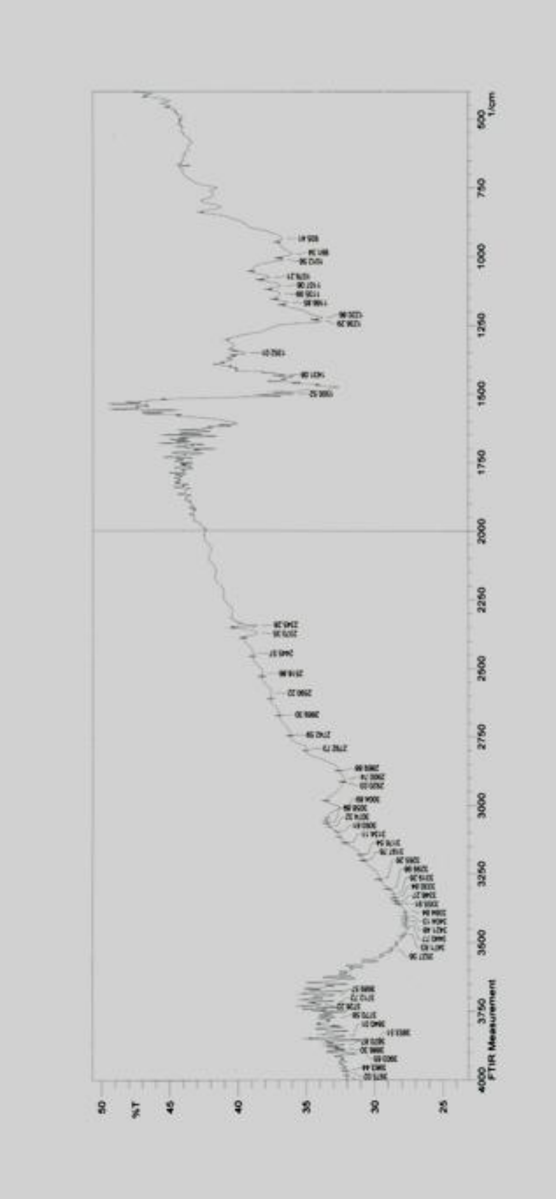


Fig.5 FT-IR Plot of Ortho Novolak Resin without Methanol addition Sample (1).

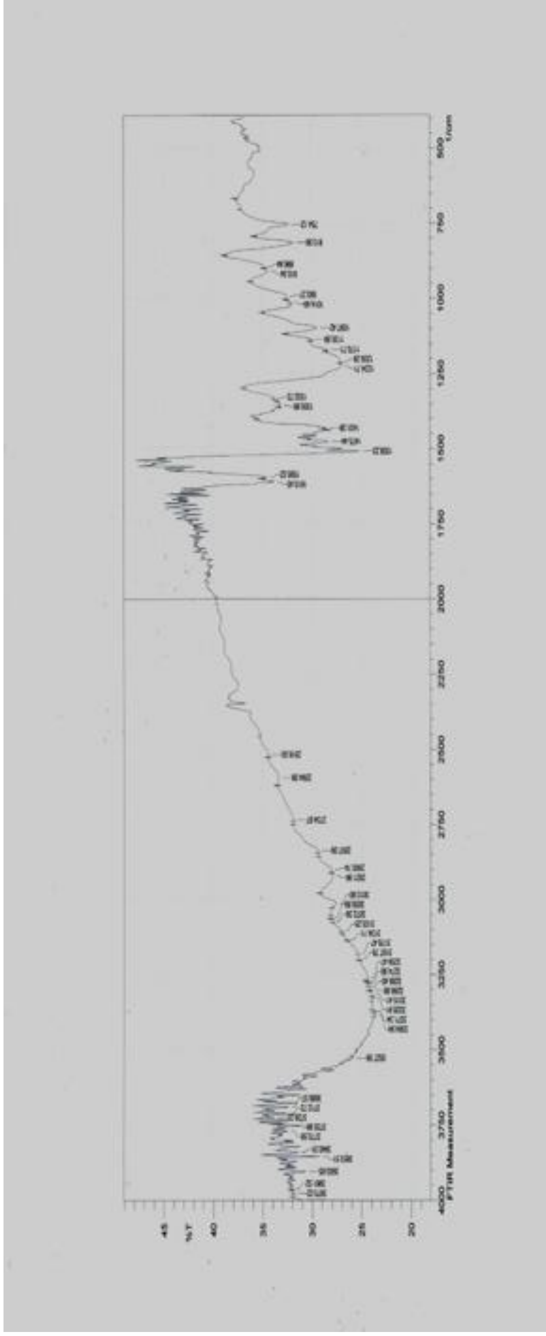


Fig.6 FT-IR Plot of Ortho Novolak Resin with Methanol addition Sample (3).

## Conclusions

1. Experimental determination using FT-IR and UV-Spectroscopy showed that on the addition of 30% of methanol and according to the second mechanism of addition, lead to the increase of shelf life to 12 months without obvious decomposition and color change.
2. It is suggested that methanol plays an important role in the inhabitation of the reactive sites on the resin which are responsible for the oxidation of the polymer when exposed to atmospheric or storage condition.

## Nomenclature

| | |
|---|---|
| A | moles of Catalyst |
| F | moles of Formaldehyde |
| P | moles of Phenol |
| W | moles of Water |
| λ | Absorbed light of UV-Spectroscope |

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