

Synthesis of Ketonic Resin and Its Industrial Applications

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Abstract:

In this paper a process for preparing ketone-formaldehyde resins, especially Cyclohexanone-Para formaldehyde resins is discussed below for producing a pale colored resin compared with others resins. A Reactive Ketonic resin was prepared by taking $(N + 1)$ moles of Aldehyde component to the N moles of Ketone, this is done to produce methylol connections, $-CH_2OH$ terminals on the cyclohexanone's α carbon. A smooth reactor system is designed to conduct the reaction of ketonic resins with catalyst 10% NaOH, varying ratio of ketone to catalyst charge .from 0.0958 to 0.1289. In this paper there is observation of product formed. A pale colored resin compared, $-CH_2OH$ terminals on the cyclohexanone's α carbon., ketonic resins with catalyst 10% NaOH.

Introduction:

This article details about the known ketones or mixtures of ketones and aldehydes that can be converted to resinous products in the presence of basic catalysts or acids. For instance, resins can be prepared from mixtures of cyclohexanone and methyl cyclohexanone (Ullman's Encyclopedia of Industrial Chemistry, Vol. 12, p. 551). Cyclohexanone and formaldehyde react to give hard resins which find use in the coatings industry. Processes for preparing such products are described, for example, in U.S. Pat. No. 2,540,885^[1], U.S. Pat. No. 2,540,886^[3], DD 12433, DE 13.00256, DE 2831613, DD 123481 and DE 1256898, all listed references are incorporated by reference, According to DE 2831613, Poly-condensation products are obtained from aliphatic or cyclic ketones or mixtures of these ketones with aliphatic aldehydes in the presence of basic catalysts using from 0.005 to 10 mol %, based on the total amount of ketone and aldehyde, of a phase transfer catalyst. It is known to those skilled in the art that the process disclosed there can only provide resins having very high softening points and, as a result, high molecular weights.

Since one use of the resins is in the coatings industry to reduce the solvent fraction, such high molecular weights are particularly disadvantageous. It is also known to those skilled in the art that cyclohexanone-formaldehyde resins lose their broad solubility properties at an excessively high molecular weight. Moreover, it is known to those skilled in the art that resins according to the processes described have low non-volatile fractions, which can have a negative influence on the thermal stability, and the yields of the process described

are low. It is also known that methyl ketones and cyclic ketones add to formaldehyde under preferably basic conditions to form the corresponding methylol compounds (stage 1).

Depending on the pH and temperature. Such methylol compounds dehydrate to form the corresponding vinyl ketones (stage 2). Under basic conditions, vinyl ketones in turn add to active hydrogen's of the ketones by the mechanism of Michael addition, resulting in ketone-formaldehyde resins as the end product (Stage 3).

In such processes, formaldehyde is used in the form of 30 to 37% aqueous solutions. The catalyst consists of 50% aqueous Sodium hydroxide solution or potassium hydroxide solution or a mixture of aqueous alkali and phase transfer catalyst. The use of aqueous solutions and, for example, of sodium hydroxide Solution greatly restricts the process in several respects:

- (1) The ketones only have a limited solubility in water, so that, to achieve adequate reaction rates, large amounts of methanol or ethanol have to be used as solubilizers. These solvents reduce the space-time yield, lead to wastewater/waste air problems and are expensive to recover in a crude/purified form,
- (2) The use of sodium hydroxide Solution as a catalyst permits workup only by washing procedures which are particularly time- consuming. The necessary neutralization, for example, by means of acetic acid to give Sodium acetate, additionally makes the wastewater costs more expensive.

Accordingly, it is an object of the present invention to find a process which eliminates the above-mentioned disadvantages. In particular, the process should firstly have a higher space-time yield and simultaneously greatly reduce the amounts of Solvent and water used. Surprisingly a process for preparing ketone-formaldehyde has been found in which the aqueous formaldehyde solution has been replaced by 100% formaldehyde which is available on the market as paraformaldehyde.-

The inventive catalyst can be removed by distillation, but has a sufficiently high basicity which is obligatory for stage 1, but in particular for stages 2 and 3.

Process carried out in the preparation:

A process for preparing ketone-formaldehyde resins:

1. At least one ketone (Cyclohexanone) and
2. An aldehyde (para formaldehyde),
3. In the presence of NaOH base catalyst in the form of an aqueous solution as a catalyst, at temperatures in the range between 40 and 225° C. In an open system
4. NaOH to the mixture of paraformaldehyde and cyclohexanone at a 37 ° C, and the reaction is carried in the ranges from 42 to 210° C., preferably at 180 ° C.

MATERIALS & METHODS :

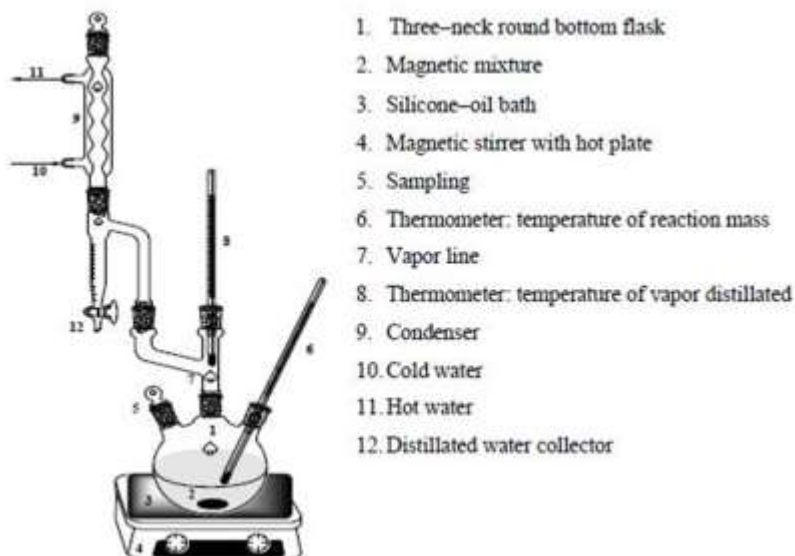
MATERIALS:

Chemicals, such as, Cyclohexanone, Para formaldehyde, were procured from Local Vendors (India) for the resin synthesis. Other chemical such as Sodium hydroxide was procured from Merck Life Science (India), m-xylene were procured Local -Vendor (India).

METHODS:

Open system procedure details:

Polymerization reactions of ketonic resin under atmospheric pressure condition were conducted in a 750 ml capacity three-neck kettle reactor, equipped with a stirrer and a Dean-Stark condenser. The reactor assembly was set in a heating mantle to maintain a constant (within increment of 1°C) temperature. A schematic diagram of the open system setup is shown in Figure. In all the runs, around 600 g was taken into the reactor and heated it to a desired reaction temperature under a stirring speed of 1000 + 20 rev/min. Once the temperature reached to the preset value, calculated amount of alkali catalyst was added into the reactor, and the reaction was continued further for the desired time duration. During the polycondensation reaction, as the water evolved is condensed with the condenser as the temperature reaches 150-160°C 5ml of Xylene is dosed to withdrawn the water from the reaction and avoiding backward or delay in reaction to forward by withdrawing products formed (such as. Water formed) at respective time interval the sample is withdrawn to observe thread formation of polymer formed. At the end of reaction time, the reaction mass was cooled to room temperature. Procured in tight sealed containers.

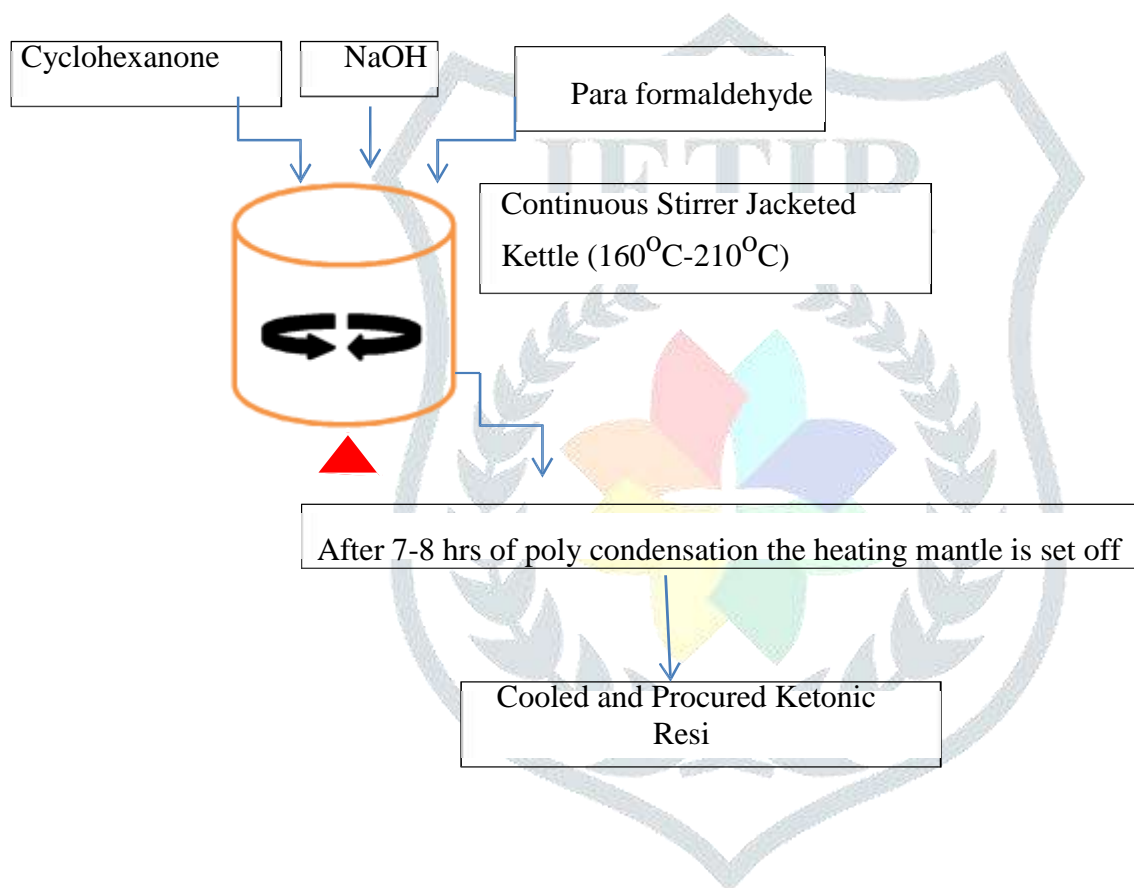


EXPERIMENTATION

A process for preparing ketone-formaldehyde resins:

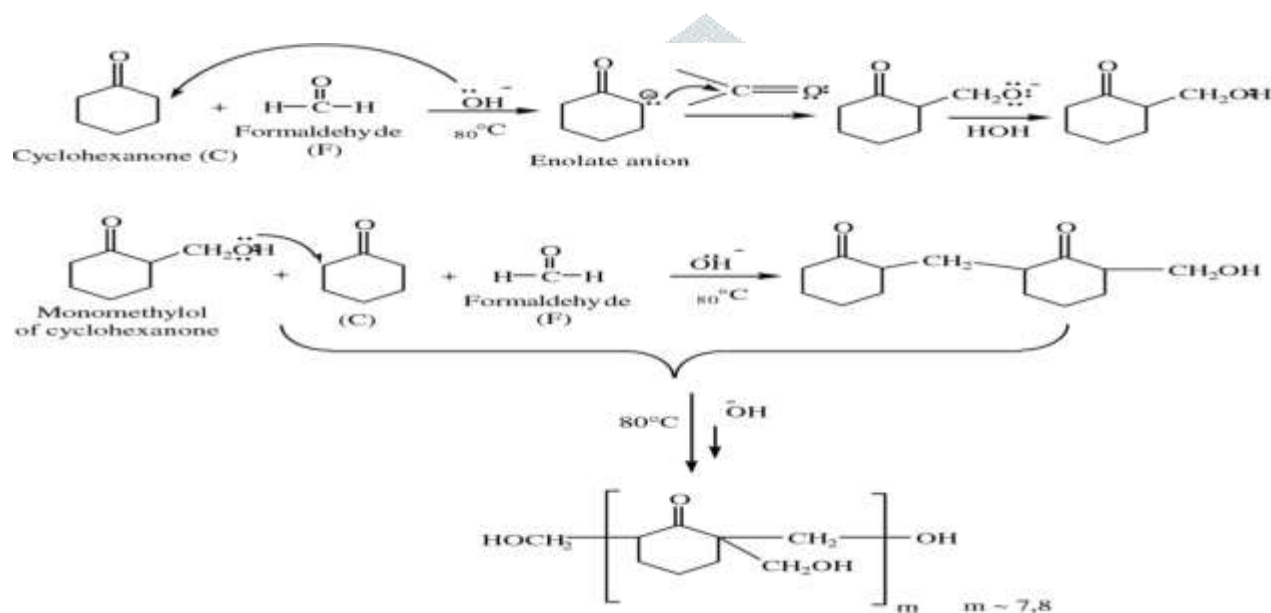
1. At least one ketone (Cyclohexanone) and
2. An aldehyde (para formaldehyde)
3. In the presence of NaOH base catalyst in the form of an aqueous solution as a catalyst, at temperatures in the range between 40 and 225° C. In an open system
4. Adding NaOH to the mixture of paraformaldehyde and cyclohexanone at a 37, and the reaction is carried in the ranges from 42° C to 210° C., preferably at 180 ° C

Block Presentation of the Ketonic resin process.



The reaction is below:

1. The first stage is the formation of enolate anion which initiates the methylol anion which is neutralized by water formed and resulting in Methylol of Cyclohexanone formation
2. The second stage is the chain elongation by the methylol compound's -OH group transfer on the α - **Carbon** of the cyclohexanone and formaldehyde in reactants to form chain a -CH₂ Group linkage. The final stage resulting in Ketonic Aldehyde Resin formation.



molar calculations:



Molar balance of above reaction is:

(n) moles of cyclohexanone + $(n + 1)$ moles of paraformaldehyde =
 $(n - 2)$ of ketonic Resin + $(n - 1)$ moles of water

For 1000 molecular weight ketonic resin:

(N) moles of Cyclohexanone + $(N+1)$ moles of Paraformaldehyde = 1000 molecular wt KR + $(N-1)$ moles of water

$$1000 = (n + 1) * 30.03 + (n) * 98.15 - (n - 1) * 18$$

$$1000 = (n) * (98.15 + 30.03 - 18) + 30.03 + 18$$

$$1000 - 48.03 = 110.18(n)$$

$$n = 8.64013$$

Accordingly, we can calculate the weight of reactants required.

Sr. No.	Wt./Moles	Cyclohexanone	Para formaldehyde	%NaOH (wt. in gm) (10%)	Color & Consistency
1	Wt. (Gms) Moles	400.27 4.078145695	133.9289 4.45983683	37.56	Sticky Solids, Light Brown
2	Wt. (Gms) Moles	399.9 4.074375955	133.86 4.457542458	39.50	Sticky Solids, Brown
3	Wt. (Gms) Moles	399.3 4.068262863	134.01 4.462537463	41.94	Sticky Solids, Transparent Brown
4	Wt. (Gms) Moles	399.37 4.068976057	133.78 4.454878455	45.03	Solids pale greenish brown colored
5	Wt. (Gms) Moles	398.59 4.061029037	134.03 4.463203463	50.3	Failure

$$n = 8.64013$$

Weight (gm) of reactants required for 1000 molecular weight of ketonic resin:

Cyclohexanone 848.016

Paraformaldehyde 289.4892

Conversion=2.929353

For, 400gm of Cyclohexanone we calculate the required amount of paraformaldehyde required

Weight (gm)

Cyclohexanone 400

Paraformaldehyde 136.5489

Below is a table formulated which details the observation of color and consistency formulations

OBSERVATION

AS FROM THE FORMULATION TABLE THE OBSERVATIONS ARE DETAILED BELOW:

1. For Wts. of 400.27gms (By Moles 4.078145695), Para Formaldehyde 133.9289 gms (By Moles 4.45983683) and % NaOH (10%) 37.56 Wt. in gms was reacted, it was observed that a Sticky mass observed at 160-180 degree, discharged at 200 degree after 4.5 hrs. Of reaction time, temperature range 38°C-206 °C. Sticky Solids, Light Brown observed after reaction time.
2. For Wts. of 399.9gms (By Moles 4.074375955), Para Formaldehyde 133.86 gms (By Moles 4.457542458) and % NaOH (10%) 39.5 Wt. in gms was reacted, it was observed that a Sticky mass

seen at 190 °C, temperature maintained in the range of 190-202 °C towards the end of reaction..Sticky Solids, Brown observed after reaction time.

3. For Wts. of 399.3gms (By Moles 4.068262863), Para Formaldehyde 134.01 gms (By Moles 4.462537463) and % NaOH (10%) 41.94 Wt. in gms was reacted, it was observed that a Addition of NaOH at 40 °C, at 180 °C sticky mass observed, reaction maintained in range 180-200 for 1 hr. towards the end, Sticky Solids, Transparent Brown observed after reaction time.
4. For Wts. of 399.37gms (By Moles 4.068976057), Para Formaldehyde 133.78 gms (By Moles 4.454878455) and % NaOH (10%) 45.035 Wt. in gms was reacted, it was observed that a Addition of NaOH at 40 °C, at 184 °C sticky mass observed, reaction maintained in range 184-203 °C for 1.5 hr. towards the end, Solids pale greenish brown colored observed after reaction time.
5. For Wts. of 398.59 gms (By Moles 4.061029037), Para Formaldehyde 134.03 gms (By Moles 4.463203463) and % NaOH (10%) 50.3 Wt. in gms was reacted, it was observed that a After addition of NaOH at 35 °C, there was a rapid rise in the temperature to 110 °C without the application of any heat, the charge was thrown out of the kettle at 120 °C due to accumulation of vapors in the kettle at a rapid rate. No color, failure.

Above table gives a brief overview of the experimentation observations, as we can infer from the table that the product formed Using < 50gm NaOH (10%) showed better results,

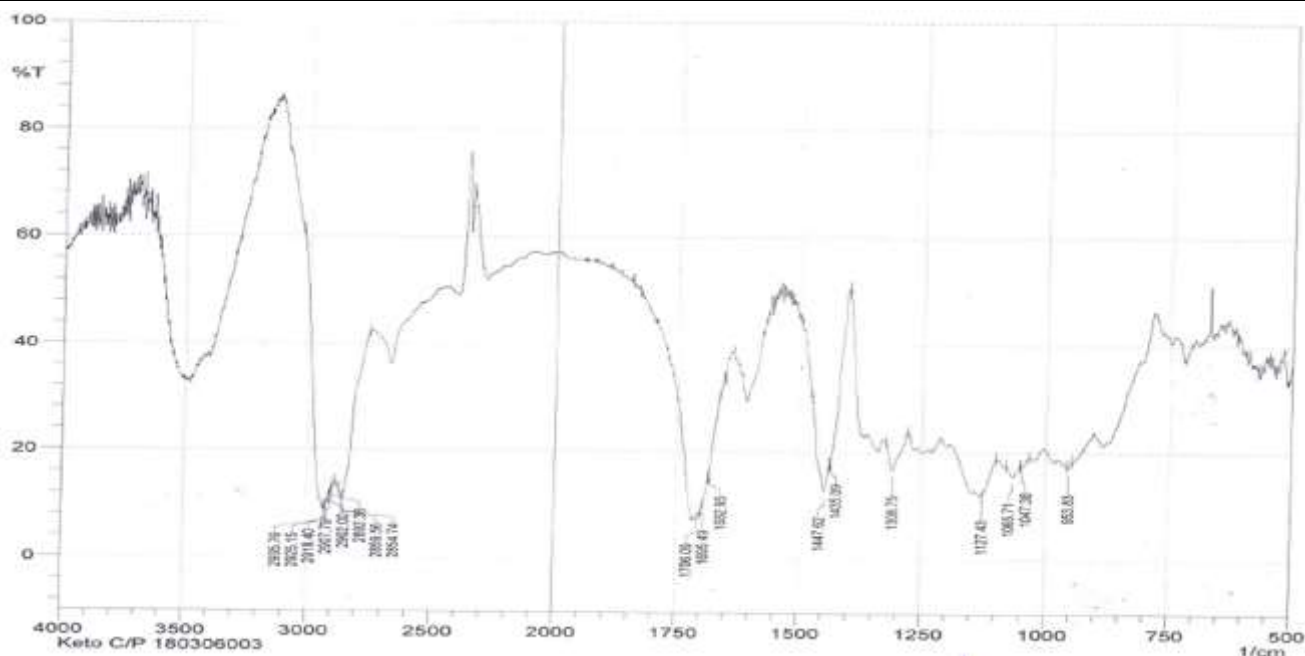
There were reactions conducted in the range of 45-50g of NaOH catalyst charge which are not mentioned in the table, but all the reactions above 45g of NaOH charge resulted in sudden rise in temperature, thrown out of reactant charge from the open reactor system.

The observed product was obtained at 41.94g of NaOH, it has the right color and consistency which was desired, and even the varnish produced had superior properties than the CSNL base varnish.

Analysis: Fourier Transform Infrared (FTIR) analysis:

Fourier Transform Infrared spectrometer at Qualichem labs was used to identify the characteristic peaks associated with -.

The resin sample mixture was made using a die set for the FTIR analysis. The FTIR spectra of the resins were recorded in transmission mode within the wavenumber range between 4000-500 cm^{-1} .



:3200 – 2700	Weak, Broad	O – H Stretching	Alcohol	Intra Molecular Bonded
1725 – 1705	Strong	C = O Stretching	Aliphatic Ketone	Cyclo hexane, Cyclo pentenone
1465	Medium	C – H Bending	Alkane	Methylene Group

APPLICATION

1. The synthetic product formed was used to produce a varnish using blends and their properties such as Drying time, Adhesion and Hardness were observed and were found to be significant.
2. The application may include using ketonic resin as a charge in alkyd resin production and its added benefits.
3. The blends of Ketonic resin and CNSL of different formulation were prepared which can be incorporated in paint varnish preparations.

*Reacting PRODUCT FORMED with CNSL (Cashew Nut Shell Liquid) and THE varnish PRODUCED, HAS better properties from drying to adhesion.

CONCLUSION

The preparation of Cyclohexanone–Para formaldehyde resin using a laboratory glass reactor with a Dean–Stark separator. Toluene (1:1) was used as solvents to dissolve the Para formaldehyde. The maintained molar ratio of ketone–to–aldehyde was one. The reactions were carried out at 95 °C for a reaction time of 4 hrs, melting point of the resin product was 140 °C.

The observed product was obtained at 41.94g of NaOH, it has the right color and consistency which was desired, and even the varnish produced had superior properties than the CSNL base varnish.

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