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# Progress in Organic Coatings

# Preparation and characterization of ketonic polymer for coating applications

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ABSTRACT

A systematic study has been performed to develop a synthetic resin from cyclohexanone by self–polymerization method in presence of a base catalyst. In addition, an effort has been made to characterize a product by analyzing its various physico–chemical properties such as hydroxyl content, iodine value, acid value, solubility, viscosity, adhesive strength, and average molecular weight. To investigate the effects of operating parameters on physico–chemical properties, reaction time was varied between 7 and 20 h, catalyst loading was varied between 0.05–0.4, and temperature was varied in the range of 90–160 °C. The extent of polymerization reaction increased with the increase of catalyst loading, reaction temperature and reaction time. A good quality resin was obtained when the reaction was performed in a closed reactor. The study confirmed that KOH offers better quality product than NaOH. The average molecular weight of the products lies in the range of 300–1200. It has been further observed that the adhesive strength of the solid resins is comparable with the commercial fivistick material. The article includes the development of mathematical model to find the product properties.

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## 1. Introduction

Synthetic resins are widely used in various fields of application including paints and plastics technology. In paint industry, resins are mostly used to improve the glossiness and adhesiveness of paints. Synthetic resins are polymeric substances, which are prepared from monomers by polymerization reaction. Most commonly used synthetic resins are epoxy resins, alkyd resins, polyamide resins, polyurethane resins, vinyl resins, acrylic resins, phenolic resins, ketone–aldehyde resins etc. Synthetic resins like phenol–formaldehyde resins are sensitive to alkaline environment, whereas ketonic resin shows more resistance to degrade under alkaline environment [1].

## 2. Previous studies in regards to using ketone and aldehyde monomers

It is known that ketones, aldehydes, or their mixtures can be converted to resinous materials in presence of an acid or a base catalyst. Reaction of cyclohexanone with formaldehyde yields a

hard resin that can be used in coating applications [2]. Melvin and Murry [3], have studied the self–condensation of various aldehydes and ketones in presence of Amberlite IR–120 and Dowex–50 as catalyst. The author found that Dowex–50 offered comparatively better conversion over Amberlite IR–120. Takashi and Kazuo [4], have studied the kinetics of self-condensation of cyclohexanone to yield 2–(1–cyclohexenyl) cyclohexanone in presence of sodium ethoxide catalyst at a temperature range of 0.6–10 °C and a pressure range of 1–2000 kg/cm$^2$(g) using a high pressure apparatus. The report says that the activation energy for the dimerization reaction is around 53.2 kJ/mol. Muzart [5], has studied the self–condensation reaction of cyclopentanone and cyclohexanone in presence of basic aluminium oxide ($Al_2O_3$) at room temperature. The objective of the study was to prepare a dimer product. Jose et al. [6], have studied the kinetics of self–condensation of cyclohexanone in presence of Amberlyst–15 catalyst at a temperature range of 70–110 °C. It was reported that the conversion of cyclohexanone was around 35% more when the condensed water was continuously removed from the reaction mixture. Yogesh et al. [7], have studied the self–condensation of cyclohexanone to yield dimer, trimer and tetramer products in presence of different acidic ion exchange resin catalysts such as Amberlyst–15, Amberlyst–45, T–63, T–66, ZSM–5 and Zeolite β at a temperature range of 80–100 °C under atmospheric pressure. The author

observed that both T–63 and Amberlyst–45 catalysts offered better conversion of cyclohexanone. Yeqiang et al. [8], have studied the kinetics of the reversible dimerization reaction of cyclohexanone in presence of γ–alumina catalyst at a temperature range of 110–130 °C. The Langmuir–Hinshelwood kinetic model was used to describe the dimerization reaction of cyclohexanone. It was observed that accumulation of condensed water within the reaction media shows a negative effect on rate of dimerization reaction. David et al. [9], have studied the kinetics of dimerization reaction of self–condensation of cyclohexanone in presence of sodium hydroxide (NaOH) catalyst. The study was performed in the temperature range of 125–150 °C and around 80% monomer conversion was obtained.

Hurst et al. [10], have patented a process to prepare a ketone–aldehyde resin by reacting cyclohexanone and/or methyl cyclohexanone with formaldehyde in presence of NaOH at a temperature range of 70–100 °C. According to the disclosure, the author prepared a colorless resin with melting point range of 75–90 °C. Rainer et al. [11], have disclosed a process to produce a ketone–aldehyde resin which can be used in paint application. The polymerization reaction was carried out under atmospheric pressure in presence of NaOH along with various phase transfer catalysts (PTCs). The presence of PTC, the softening points of the products increased approximately by 30%. Martina et al. [12], have disclosed a process for the preparation of ketone–aldehyde resins through condensation reaction of ketone (cyclohexanone, 4-tert-butyl cyclohexanone, methyl ethyl ketone, acetophenone etc.) with formaldehyde in presence of NaOH. Solubility test of the developed resins in various solvents such as ethanol, n-butanol, butyl acetate, xylene, mineral oil etc. and compatibility test with various binders and resins were extensively studied in the work. Kizilcan and Koşar [13], have studied the synthesis of carbazole modified ketonic resins, such as, cyclohexanone-carbazole-formaldehyde, and acetophenone-carbazole-formaldehyde resin. It is mentioned that carbazole modified ketonic resins offered better fluorescence and solubility properties compared to cyclohexanone-formaldehyde ketonic resin. Ustamehmetoğlu et al. [14], have studied the corrosion inhibition and photoactivity effects of different types of ketonic coating materials, such as, polyvinylcarbazole, polyvinylcarbazole methyl ethyl ketone formaldehyde, carbazole methyl ethyl ketone formaldehyde, and polycarbazole methyl ethyl ketone formaldehyde resin. Among the studied materials, carbazole modified methyl ethyl ketone formaldehyde resin offered better performance towards corrosion inhibition.

Poly–cyclohexanone resin was first patented by BASF in 1930. In 1937, "Winton Picture Varnish" was formulated with poly–cyclohexanone and unknown plasticizers to overcome the brittleness of the paint film. Different varieties of ketonic resin such as Laropal K80, MS2, AW2, and Ketone Resin–N etc. are available in the market for paint application [15,16]. Dinda et al. [17], have studied the self–polymerization reaction of cyclohexanone using a high pressure reactor to prepare a solid resin. The presence of a specific functional group in polymer is useful to modify the physico–chemical properties like adhesiveness, solubility, and film–forming ability of the polymer. Hydroxyl content in a polymer is also an important characteristic to analyze the degree of polymerization. The reactivity of the hydroxyl group plays a vital role on film formation properties of a resin [18].

Statistical techniques provide an effective, efficient and faster determination of the system behavior. Mathematical and statistical techniques are useful for developing, improving and optimizing the processes [19,20].

From the aforementioned literature survey, it has been observed that most of the studies were carried out on dimerization reaction of cyclohexanone or alkyl cyclohexanone. Very few studies

are available in the literature on oligomerization or polymerization of cyclohexanone/alkyl cyclohexanone with aldehyde (mainly formaldehyde) to obtain a ketone–aldehyde resin. It is also observed that most of the polymerization or self–condensation study was carried out in presence of NaOH as base catalyst and not with KOH. In addition, there is scanty information in the literature about the characterization and analysis of various properties of a product. However, for the commercial utilization of any product requires a systematic study, which has not been reported in majority of the literature. Therefore, in the present work, our objective is to develop a synthetic ketonic resin from cyclohexanone using a base catalyst such as KOH or NaOH. The other objective is to establish a suitable analysis procedure to characterize a resin product. The advantage of using cyclohexanone as the starting material is that it is not carcinogenic in nature and itself offers an excellent candidate for the development of ketonic resin, and it has the potential to replace the more hazardous materials like phenolic and aldehyde compounds.

## 3. Experimental details

### 3.1. Materials

Raw materials such as cyclohexanone, NaOH, KOH and other analytical reagents such as methanol, ethanol, ethyl acetate, butanol, chloroform, glacial acetic acid, iodine trichloride etc. were procured from S D Fine–Chemicals Ltd. (India). Few analytical reagents such as toluene, pyridine were procured from Fischer Scientific (India) and acetic anhydride, mineral turpentine oil (MTO) were obtained from Hychem Laboratories (India).

### 3.2. Experimental procedure

Polymerization reactions under atmospheric pressure (open system) were conducted in a 250 ml capacity three–neck glass reactor, equipped with magnetic stirrer and Dean–Stark condenser. The reactor assembly was set in a thermostatic oil bath to maintain a constant (within ±1 °C) temperature. Closed system polymerization reactions were conducted in a Parr reactor. The reaction time was varied from 7 h to 20 h. At the end of reaction time, the reaction mass was washed with water to remove the alkali from product mass and dried using a hot air oven. The dried samples were used for measuring its various physico–chemical properties like moisture content, acid value, iodine value, hydroxyl value, solubility, viscosity, and average molecular weights. To check the repeatability, few runs were performed in duplicate and around 1–3% experimental error was observed in experimental analysis.

### 3.3. Instrumental analysis

Gas Chromatography (Agilent, 7820A) with FID and HP–5 column was used to estimate the monomer conversion. Matrix Assisted Laser Desorption Ionization Time–of–Flight (MALDI–TOF) Mass Spectrometer (Shimadzu Biotech AXIMA Performance) was used to find the average molecular weight of the product samples. Karl–Fischer Titrator (Systronics, India, KF Titrator–349) was used to find the moisture content in the final products. Brookfield made R/S Plus Coaxial Cylinder Rheometer was used to find the viscosity of the final product. To identify the characteristic bands associated with different functional groups, Fourier Transform Infrared Spectroscopy (FTIR) spectra of the products were recorded in transmission mode by using FTIR spectrophotometer (JASCO, Japan, Model No. 4200) in the wavenumber interval between 4000 and 400 cm$^{-1}$.