Chapter-II

Experimental

Ambersep 900(OH^-)

The strong basic anion exchange resin was used as polymer support; the basic anion exchange resin being in $\bar{O}H$ form, Ambersep 900, was purchased from Acros Organics Company. The basic resin hydroxide styrene cross linked with DVB. The structure of Ambersep 900 ($\bar{O}H$) was Macroreticular having decomposition temperature 140^0 F, composition is approximately 35-55% quaternary amine divinyl benzene /styrene copolymer of $\bar{O}H$ form and 45-65% water.

The polymer supported chromium (VI) oxide (including polymer, Ambersep 900(OH^-), 4%, 6% and 6.5% quaternary ammonium anion exchange resin) acts as a new class of recyclable solid phase oxidizing agent.

Material and purity:

The double distilled water was used throughout the work, obtained by redistillation of distilled water in the presence of few crystals of $KMnO_4$ and few pellets of KOH using corning glass distillation assembly.

Ambersep 900(OH^-) was purchased from Acros Organics. The 4% and 6.5% chloromethylated polystyrene beads were supplied by Thermax Private limited, Pune, as a gift sample.

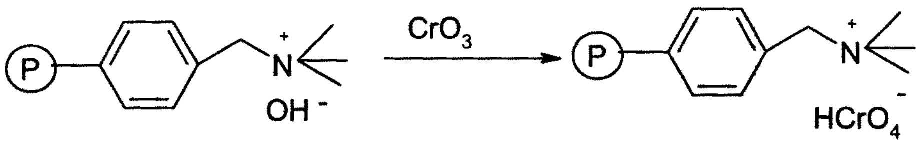
All the chemicals used during the investigation were AR grade, alcohols were purified before use.1:4Dioxane, carbon tetrachloride, chloroform, cyclohexane and trimethyl amine were of spectroscopic grade.

Preparation of polymer bound Chromium (VI) oxide:

Various techniques have been employed for impregnating the oxidizing agent on different supports. The most commonly used technique is the 'Wet impregnation' method in which the oxidizing agent is first dissolved in a suitable solvent and mixed with the solid support. The solvent is vaporised to get the oxidizing agent impregnated on the solid support.

In the 'Dry method' the oxidizing agent and support are thoroughly ground together. This is commonly known as dry dispersion.

In the present work, to prepare the reagent[1-3] 10 gms of the hydroxide form of Ambersep 900(OH^-), a macroreticular anion exchange resin, containing quaternary ammonium group was stirred with saturated aqueous solution of 5 gms of chromium trioxide in 30 ml of water for 30 minutes at room temperature, using a magnetic stirrer. Hydroxide ions were readily displaced and $HCrO_4^-$ form of the resin was quantitatively obtained in 30 minutes.

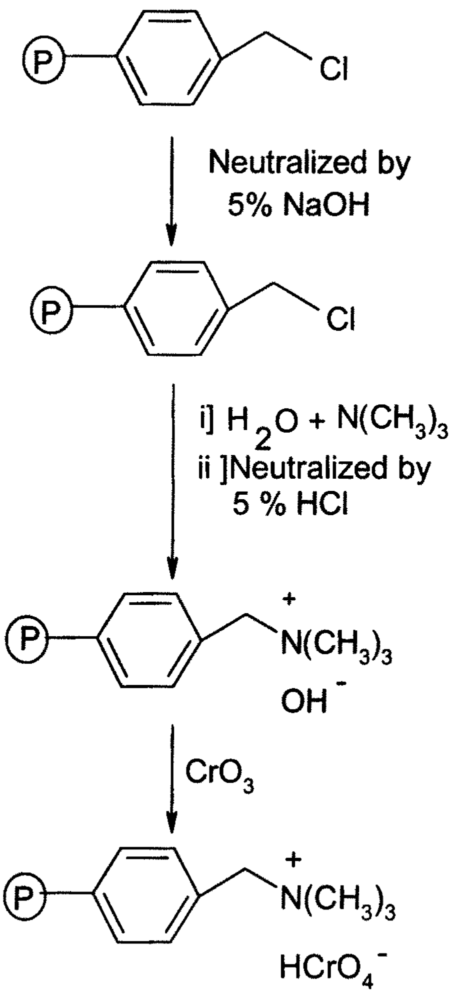


The resin was successfully rinsed with water, acetone, ether and finally dried in vacuum at 50°C for 5 hours. The dried form of the resin was stored and used throughout our study.

Ambersep 900 supported with Chromium (VI) oxide is used as a oxidant. In order to study the effect of crosslinking on the rate of reaction a polymer supported Chromium (VI) oxide was prepared from 4% and 6.5% Chloromethylated polystyrene.

Preparation of 4% and 6.5% crosslinked polymer supported chromium (VI) oxide.

First 50 gms of Chloromethylated beads were neutralized with 5% sodium hydroxide and then stirred with 30 ml water and 60 ml Trimethyl amine for some time, after that it was neutralized with 5% hydrochloric acid then the resin is treated with chromium trioxide as mentioned in above procedure and the 4% and 6.5% crosslinked polymer supported chromium (VI) oxide was formed.



Determination of capacity of polymeric reagents:

The capacities of chromate form of Ambersep 900 (4%, 6% and 6.5%) were calculated by iodometric method. The 0.5 gm of resin was stirred overnight with 10 ml of 2N aqueous potassium hydroxide, filtering off to obtain chromate solution. The obtained chromate solution was used for titration. The determined average capacity of the dried resin was,

Chromate form of polymeric reagent	Capacity mmol/gm
6.5% cross linked	6.50
Ambersep 900[6%]	6.55
4% Cross linked	6.70

The same sample of polymeric reagent was used throughout the kinetic study because the resin did not looses activity on standing in air at room temperature for several weeks, nor on refluxing for 5 hours in benzene or hexane.[4]

Stability of shelf life funionalized polymer supported Chromium (VI) oxide resin:

The resin obtained in the form of fine beads was found to be stable under the ordinary laboratory conditions. The reagent can be stored indefinitely without appreciable loss in the capacity.[4] In order to determine the stability of reagent, it was kept with calcium chloride in vacuum at room temperature for period of three months and the capacities were determined by same procedure.

Stability of PS-Supported Chromium (VI) Oxide

Polymeric reagent	Initial capacity mmol/CrO3/gm	Capacity after weeks(mmol/gm)					
		2	4	6	8	10	12
4% supported Cr(VI) Oxide	6.70	6.70	6.70	6.70	6.65	6.65	6.65
Ambersep900 supported Cr(VI) Oxide	6.55	6.55	6.55	6.55	6.50	6.50	6.50
6.5% supported Cr(VI) Oxide	6.50	6.50	6.50	6.50	6.45	6.45	6.45

Regeneration of PS-Supported Chromium (VI) Oxide resin:

The easy recovery of the polymer makes it possible to regenerate and reuse. This is very important from an economic point of view, because polymer supported reagents are generally more expensive than the analogous non supported reagents.

The chromium (VI) oxide supported on Ambersep, (4%,6% and 6.5%) resin can be regenerated by washing with 0.2M sodium hydroxide to remove chromium species and subsequent treating with chromium trioxide. The capacities were determined after each regeneration by same procedure. However the spent reagent could be recovered by simple filtration and reused. The observation indicates that the above functionalized resin can be regenerated and reused.

Polymeric reagent	Initial capacity mmol/CrO3 /gm	Capacity of regenerated resins after weeks(mmol/gm)					
		2	4	6	8	10	12
4% supported Cr(VI) Oxide	6.70	6.70	6.70	6.65	6.65	6.60	6.60
Ambersep 900 Supported Cr(VI) Oxide	6.55	6.55	6.50	6.50	6.45	6.45	6.40
6.5% supported Cr(VI) Oxide	6.50	6.50	6.45	6.45	6.40	6.40	6.40

Method of following the kinetics:

Spectrophotometric method is used for kinetic study.

The main features of the experimental method are as follows.

1] The wavelength of all the alcohols under study were determined by diluting 1 mg of sample of alcohol in 100 ml of 1:4Dioxane as a reference. The wavelengths determined are as follows.

Alcohols	λmax nm	Aldehydes	λmax nm
Benzyl alcohol	258	Benzaldehyde	248
4- Methoxybe-benzyl alcohol	276	4-Methoxy benzaldehyde	273
4-Chlorobenzyl alcohol	268.4	4-Chloro benzaldehyde	254

2] The standard glass wares were used throughout the experimental work.

3] The reaction was carried out in a stoppered round bottom flask.

4] The temperature of the reaction mixture was kept constant by immersing the stoppered round bottom flask in constant temperature bath at 45°C.

5] The calculated amount of alcohol was then added in 5ml of 1:4Dioxane and a known amount of polymeric reagent was added.

6] The reaction mixture was stirred on magnetic stirrer at constant rate.

7] The standard run was carried out in 1:4 Dioxane and the completion time was monitored with the help of TLC. The reaction goes to completion within two hours.

8] At different time interval 10 μl of reaction mixture was withdrawn using Qualigen(Glaxo) 5-50 μl micropipette. Care was taken that no solid particles were removed along with the aliquot.

9] The aliquots thus withdrawn were taken in stoppered test tubes containing 5ml 1:4Dioxane, measured accurately with the help of standard measuring flask.

10] The optical densities [O.D.] of reaction mixture thus withdrawn were measured at different wavelengths corresponding to wavelength of product aldehyde, using ELICO SL-159 UV-VIS Spectrophotometer and keeping the zero time reading as reference.

The kinetic study is carried out by studying various effects of,

1] Change in concentration of substrate [i.e. alcohol]

2] Change in concentration of polymeric reagent

3] Change in solvent

4] Change in temperature

5] Change in % of crosslinking in polymeric reagent.

Test for free radical:

Initiation of reaction was done by mixing oxidant, alcohol and solvent at 45°C with continuous stirring. After 30 minutes, the reaction mixture was withdrawn in a test tube and acrylonitrile was added. The mixture after dilution with distilled water, formed a copious precipitate. The precipitate formed, due to polymerization of acrylonitrile, indicates formation of a free radical in the reaction, and also it was confirmed by precipitation with acidified methanol.

Product analysis:

The product formed, were analyzed by its 2:4 Dinitro phenyl hydrazone derivatives and IR spectra. For product analysis 5 ml of 1:4 Dioxane, 140 mg of polymeric reagent and 15μl alcohol was stirred on magnetic stirrer at 45°C.After completion of reaction (2hr.),the resin was fitered off, washed with solvent (5ml) and the product was isolated by evaporation of filtrate under reduced pressure.

The melting points of the 2,4dinitrophenyl hydrazones were as follows,

Benzaldehyde : 236°C

4-Methoxy benzaldehyde: 252°C

4-Chloro benzaldehyde : 265°C

IR spectra (Figure 1) of Benzaldehyde shows bands at,

1] 2820.03 and 2737.71cm-1 due to –C-H stretching .

2] 1702.07 cm-1 due to -C =O streching

IR spectra (Figure 2) of 4-Methoxy benzaldehyde shows bands at,

1] 2840.92 and 2740.16 cm-1 due to two –C-H stretching.

2] 1683.27 cm-1 due to -C =O streching

3] 1260.16 cm-1(s) and 1024.92 cm-1 due to –C-O streching

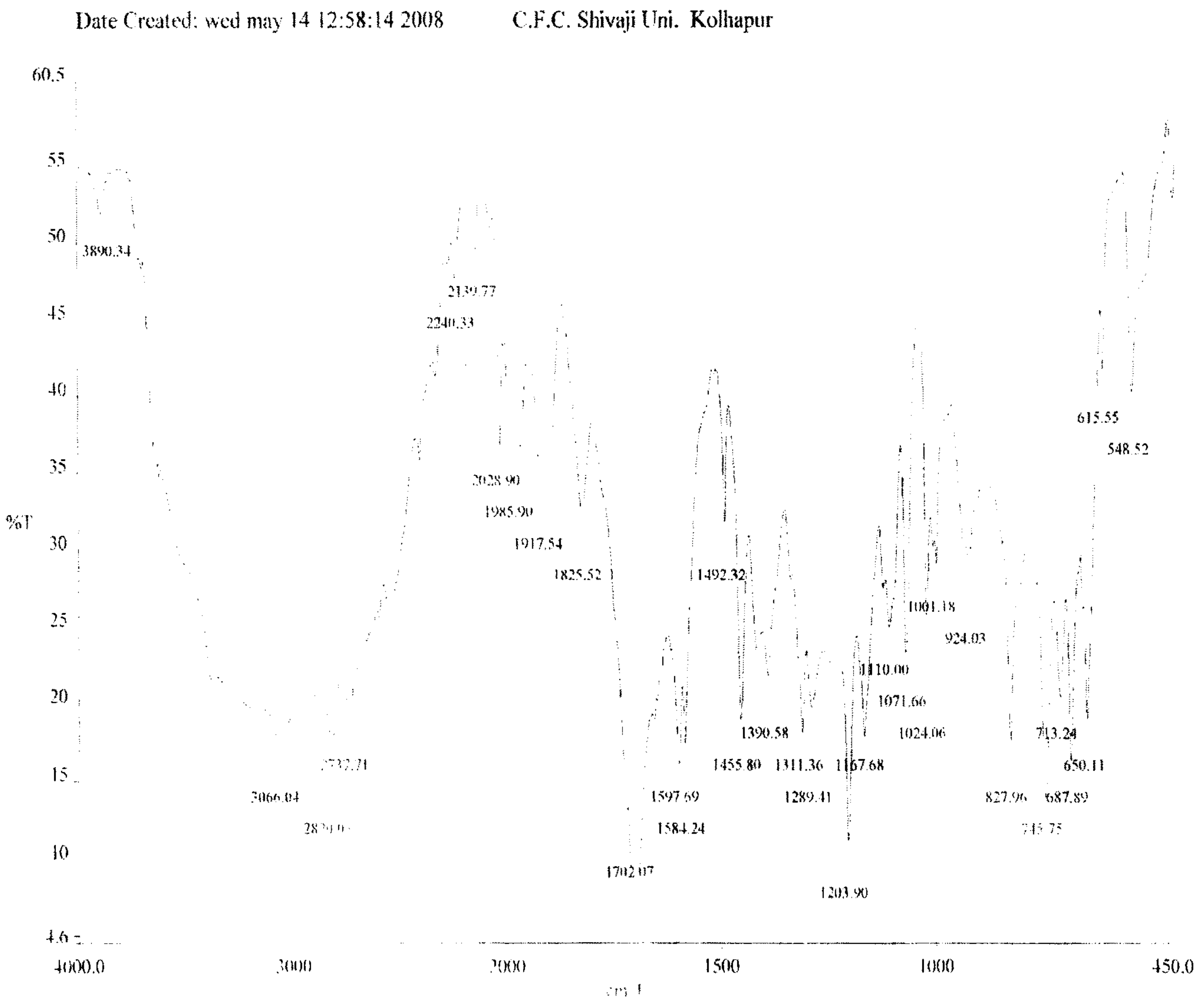
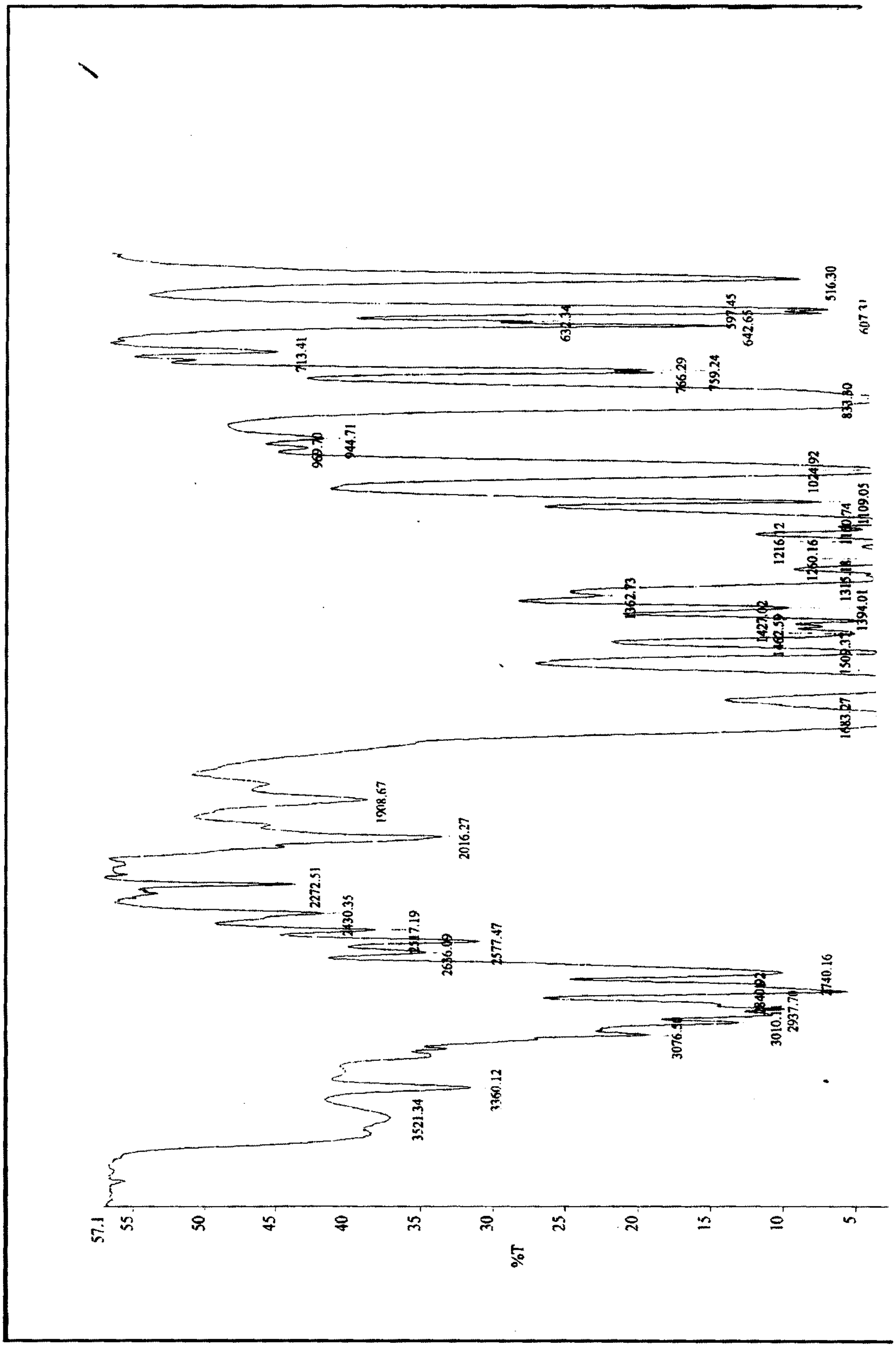

Date Created: wed may 14 12:58:14 2008
C.F.C. Shivaji Uni. Kolhapur
60.5
55
50
45
40
35
30
25
20
15
10
4.6
%T
4000.0
3000
2000
1500
1000
450.0
cm-1
3890.34
3066.04
2732.71
2240.33
2139.77
2028.90
1985.90
1917.54
1825.52
1702.07
1597.69
1584.24
1492.32
1455.80
1390.58
1311.36
1289.41
1203.90
1167.68
1110.00
1091.18
1071.66
1024.06
924.03
827.96
713.24
687.89
650.11
615.55
548.52

Figure 1



57.1
55
50
45
40
35
30
25
20
15
10
5
%T
3521.34
3360.12
3076.58
3010.11
2937.70
2840.92
2740.16
2636.09
2577.47
2517.19
2430.35
2272.51
2016.27
1908.67
1683.27
1509.37
1462.59
1427.02
1394.01
1362.73
1315.18
1260.16
1216.12
1180.74
1109.05
1024.92
969.70
944.71
833.80
766.29
759.24
713.41
642.65
632.34
597.45
516.30

Figure 2

References

1. R.O.Hutchins,N.R.Natale,W.J.Cook,*Tetrahedron Lett.,***4167**(1977).
2. K.Geethakumari,K.Sreekumar,*J.Appl.Polym.Sci.*,**67**(5), 799.
3. A.Marchaj,*Stasicka,Z.Pol.P.I.*,**124**(1984)451;(Chem.Abst.101 (1984) 71817 m).
4. G.Cainelli, G.Cardillo,M.Orena, S.Sandri,*J.Org.Chem. Soc.*,**98** (1976) 6737.
5. T.Brunlet, C.Jouitteaue, G.Gelhard, *J.Org.Chem.*, **51**(1986) 4016.
6. A.J.Buglas,S.John,Waterhous,*J.Chem.Education*,**64**(4)(1987) 712.

AMBERSEP 900

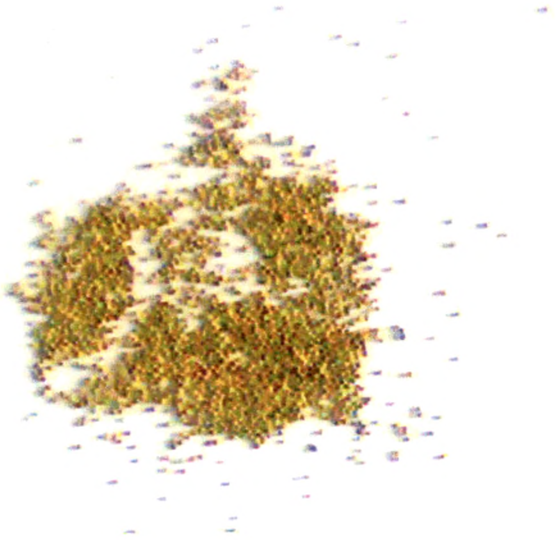
HYDROXY FORM

CHROMATE FORM

6.5% CROSSLINKED RESIN

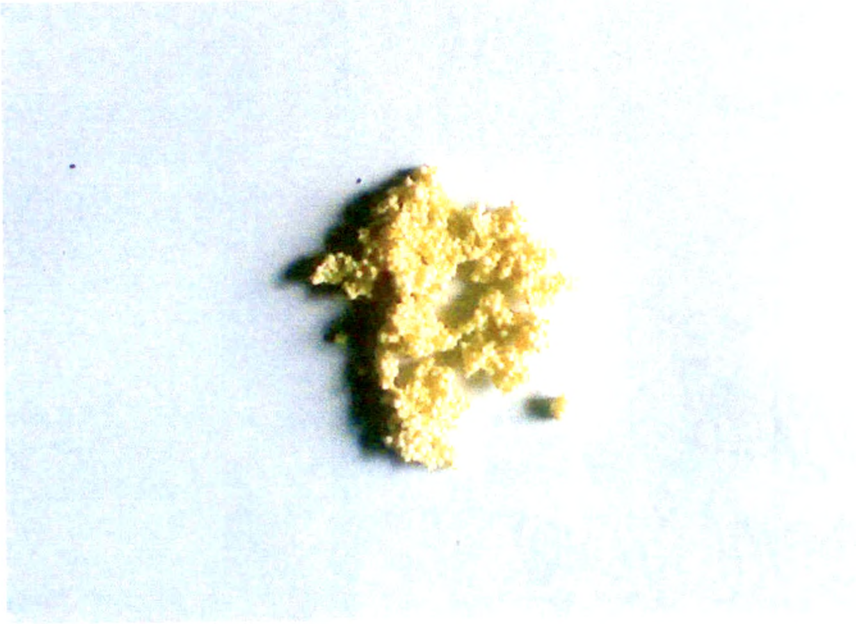
HYDROXY FORM

CHROMATE FORM



4% CROSSLINKED RESIN

HYDROXY FORM



CHROMATE FORM