Study on the Soluble Properties of Binder Resins

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Abstract

In this paper, a positive thermal imaging coating was made up of a novolak resin as the binder, dissolution inhibitor and accelerator resins, infrared dye and thermal acid generator, and its imaging property was systematically investigated. The results showed that the infrared dye acted not only as infrared absorber but unexpectedly as a strong dissolution inhibitor in the coating. Dissolution rate of the binder resin in aqueous alkaline decreased with increasing dye concentration and the imaging coating became undevelopable when the dye concentration was over 3%(wt). This effect was believed to come from the ionic structure and strong interaction of the dye with the binder resin, and contributed significantly to the inherent aging of the coating.

Keyword: thermal laser imaging, aqueous alkaline dissolution, infrared dye, phenolic resin

Introduction

With the rapid growth of CTP technology, CTP plate, a part of this technology, has made great progress. According to the principle of imaging, CTP plate can be divided into photosensitive and thermal sensitive plate. Now, thermal CTP is in the predominance position in the market, and is recognized as the most prospective printing material and has a wide market prospect in 21 century [1, 2].

According to the plate type, thermal CTP plate can be divided into negative, positive and free of treatment plate. Among of them, the imaging principle of positive plate is like this: before exposure, the resin reacts with inhibitational/accelerational matter by hydrogen bonding , resulting in that its linear molecules turn into space network structure by crosslinking, so the film-forming resin can not easily soluble in lye. When exposuring, infrared dyes at the exposured area can absorb the light energy effectively and turn it into thermal energy which promotes thermal acid generator decompositing into proton acid. With the catalytic role of the acid, the resin will decompose because of unlock of the hydrogen bonding, which destroys the space network structure into linear structure, and increases its solubility in lye. Meanwhile, with the effect of hydrogen ion, the ether bond of inhibitational/accelerational matter will be cracked. Phenolic hydroxyl deprotection produces alkali soluble substances with hydroxyl groups [3]. In the process of development, the exposured area is dissolved, appearing the hydrophilic base which is blank part; the other areas, which have no alkali-soluble because of the decomposition, stay on the base and become graphic part which is oleophilic[4].

In this paper, we select the crystal violet as indicator, and use Lambert-Beer law to investigate the dissolving laws of resorcinol resin and mix phenolic resin when they are in lye and how inhibitational/accelerational matter and infrared dyes affect the alkali-soluble of resin, then select the film-forming resin, which has the alkali-soluble performance.

Experimental

Reagents and Instrumentals

Experiments: ultraviolet spectrophotometer UV-PC, Japanese shimadzu corporation; Heating and Drying Oven DHG−9240A, Shanghai Yiheng Co, Ltd.

Materials: resorcinol resin, mix phenolic resin, inhibitational/accelerational matter, infrared dyes, crystal violet, glycol ether, developer of PS plate

Preparation of Imaging System

Make the resin of solid content of 20%(wt%) dissolve into glycol ether, and evenly coating the solution on the degreased glass substrates, and put it into 100℃ drying open oven for 10 minutes, and then put the dried sample in room temperature for 24 hours before testing.

Measurement of Imaging Performance

When dissolving the film-forming resin, unit mass of sample correspond to same amount of solution and dissolved at a fixed time. Then, using UV spectrophotometer to test the each interval absorbance Abs until the resin completely dissolved.

Lambert-Beer law: When a bunch of parallel monochromatic light through out dilute solution containing absorbing substrate, the absorbance of solution is proportional to the concentration of the absorption material and the thickness of liquid layer. Formula is as follows:

$$Abs = \varepsilon C l$$

ε is a const, concerned with the properties of absorbing material, the wavelength of incident light and temperature; C is the concentration of absorbing material; l is the thickness of liquid layer and is also a const.

According to Lambert - Beer law, when dissolving the sample into the same amount of solution, the dissolving thickness of the resin is proportional to the concentration of the resin dissolved in developer. Because ε and l is const, the dissolving thickness of the resin is proportional to Abs. So we can draw ΔAbs-t curve, in which ΔAbs represent Abs corresponding to the dissolving time.

From the dissolving curve, we can intuitively analyze the dissolving tendency of the resin. When the thickness of the dissolved film reach maximum and remain unchanged, it means the film has already completely dissolved andΔAbs is max.

Results and Discussion

Choosing indicator

Figure 1 shows the UV absorption spectra of the resin, developer and crystal violet. We can find that among 200~900nm ultraviolet visible bands, the main absorption peak of resorcinol resin and mix phenolic resign is about 300nm, the main absorption peak of developer is about 290nm and the absorption section of resin and the absorption section of developer are overlapping. With the effect of developer ultraviolet absorption, if testing the UV absorbance of resin at the peak, the resulting Abs is the overlap of the UV absorbance of resin and developer, so the testing Abs is bigger than the Abs of resin. It means that the Abs can not accurately reflect the dissolution characteristics of the resin. Therefore, we must choose indicator to test the dissolution characteristics of the resin indirectly.

The main absorption peaks of crystal violet is about 590 nm, its characteristic absorption peaks is obvious, and crystal violet not absorb UV light between 250~400nm, which is the absorption interval of the resin and developer. According to the analysis, we choose crystal violet as indicator [5], and indirectly reflect the dissolution characteristics of resin by testing the UV absorbance.

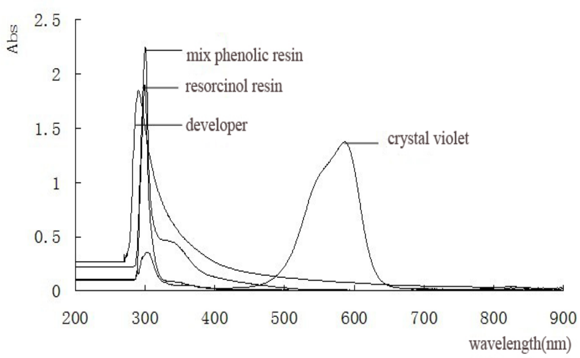


Figure1. Absorption spectra of the resin, developer and crystal violet

The dissolubility of the film-forming resin

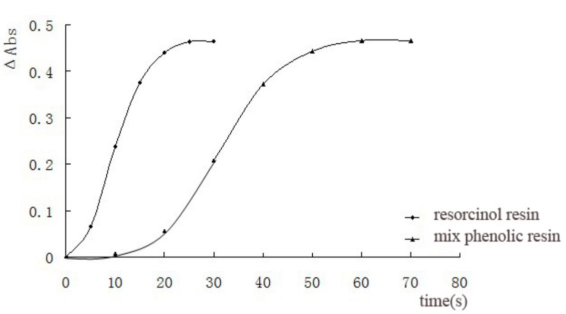


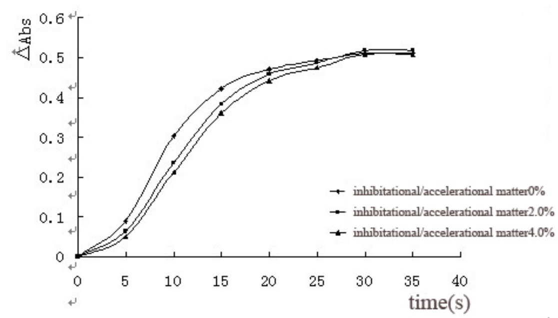
Figure2. The soluble curve of the resorcinol resin and mix phenolic resin

Figure2 shows the soluble curve of the resorcinol resin and mix phenolic resin in alkali solution. Horizontal axis is dissolving time and vertical axis is the corresponding UV absorbance. From the figure, we can see that resorcinol resin has no swell stage and quickly dissolved. After 25s, the resin on the base is completely dissolved. Mix phenolic resin has an obvious swell stage. In 10s, it can not dissolve. After 20s, it begins to slowly dissolve. After 60s, the resin on the base is completely dissolved.

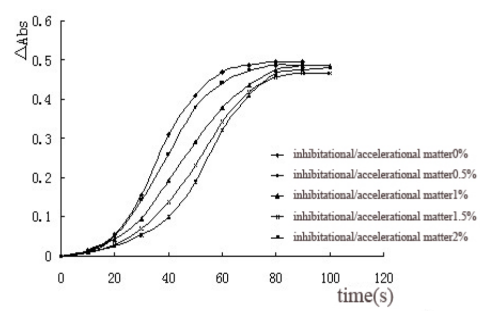
Study on the dissolution characteristics of the two resin, we find that the alkaliresistance of mix phenolic resin is higher than resorcinol resin. The difference of dissolution characteristics lies in the difference of chemical structure and different position of the substituents. So they show different dissolution characteristics [6].

The influence of inhibitational/accelerational matter on resin dissolubility

Figure3 showed the influence of inhibitational/accelerational matter on resin dissolubility. From figure 3-(a), it can be seen that when the amount of inhibitational/accelerational matter is 2.0%, 4.0%, the dissolving process of resorcinol resin is same to pure resin and there is no swell stage, and the time of complete dissolution of resin is also basically similar. The effect of inhibitational/accelerational matter on the resorcinol resin is not obvious.



(a) Resorcinol resin



(b) Mix phenolic resign

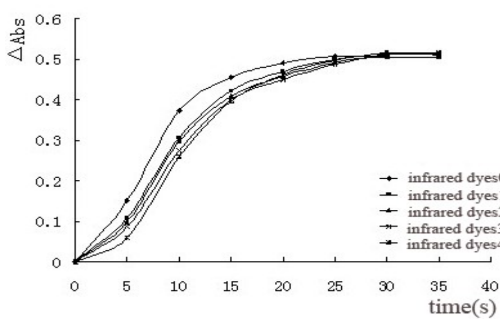
Figure3. The influence of inhibitational/accelerational matter on resin dissolubility

From figure3-(b), it can be seen that when the amount of inhibitational/accelerational matter is 0.5%, the dissolving process of mix phenolic resign is same to pure resin. When the amount of inhibitational/accelerational matter is 1.0%, 1.5% and 2.0%, the alkaliresistance of resin improve significantly. With the improvement of amount of inhibitational/accelerational matter, swelling stage become longer, and the soluble curve of resin tends to be gentle.

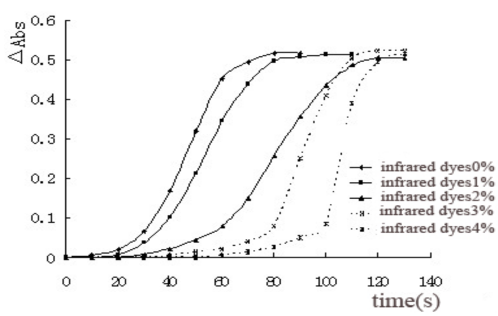
Inhibitational/accelerational matter can improve the alkaliresistance of resin. At the same time, with the increase of its content, the alkaliresistance of resin gradually improve. We find that the influence of inhibitational/accelerational matter on the dissolubility of mix phenolic resign is greater than resorcinol resin. With the increasing mass fraction of inhibitational/accelerational matter, the dissolution speed of mixed phenolic resin slows down. On the opposite, the dissolution speed of resorcinol resin is almost the same. This is because of the difference of chemical structure and the difference of alkaliresistance of the resin. Such as the strength of hydrogen bond between inhibitational/accelerational matter and mix phenolic resin is greater than that of resorcinol resin.

The influence of infrared dyes on resin dissolubility

Figure4 shows the influence of infrared dyes on resin dissolubility. From figure4 - (a), it can be seen that when the amount of infrared dye is added to 1%, 2%, 3% and 4%, the dissolving process of resorcinol resin is same to pure resin. And with the increasing of infrared dye, the alkaliresistance of resin has a slight increase.



(a) Resorcinol resin



(b) Mix phenolic resign

Figure4. The relationship between baking time and the exposure energy

From figure4 - (b), it can be seen that when the amount of infrared dye is 1%, the alkaliresistance of resorcinol resin has a slight increase. When the amount of infrared dye is more than 2%, the alkaliresistance of resin has a significant increase, and the resin is not dissolved in 60s; When the amount of infrared dye is 3%, 4%, the resin is not dissolved in 80s, after 90s, The film of resin is dropped off the film base until completely. With the increasing mass fraction of infrared dye, the alkaliresistance mix phenolic resin is great improved.

Infrared dye is able to improve the alkaliresistance of resorcinol resin and mixed phenolic resin, and with the increase of the amount of infrared dye, the alkaliresistance of resin improved. We find that because the chemical structures of the two resins are different, the effect of hydrogen bonding between infrared dye and resin is small, and the hydrogen bonding is weak, the influence of the infrared dye on the alkaliresistance of mix phenolic resin is greater than resorcinol resin. The infrared dye and mix phenolic resin have a strong hydrogen bonding association, which form a space network structure by cross-linked, and not easily destroyed by lye.

The influence of inhibitational/accelerational matter and infrared dyes on resin dissolubility

The mass fraction of inhibitational/accelerational matter is 2% and the mass fraction of infrared dye increases by equal proportional.

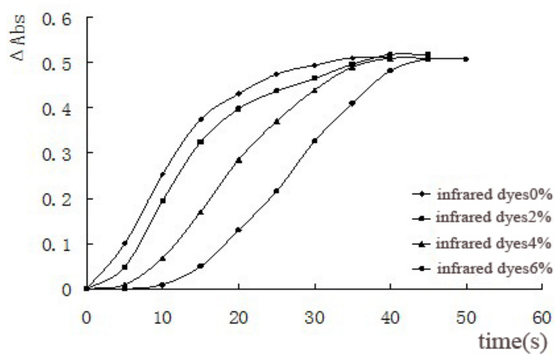


Figure5. Influence of infrared dyes and inhibitational/accelerational matter on resin dissolubility

Figure5 shows the influence of infrared dyes and inhibitational/accelerational matter on resin dissolubility. From the graph, we can see that when the inhibitational/accelerational matter remains unchanged and the mass fraction of infrared dye is 2%, the alkaliresistance of resorcinol resin improved slowly. When raised to 4% or 6%, there is a swelling stage and the speed of dissolution goes down clearly.

The mass fraction of inhibitational/accelerational matter is 1% and the mass fraction of infrared dye are0%, 1%, 2%, 3% and 4%.

When the inhibitational/accelerational matter remains unchanged and the mass fraction of infrared dye varies from0% to1%, 2%, 3% and 4%, the mix phenolic resin does not dissolve in 90s. In 100s, the film of resin drops off from the glass base with small pieces. With the dissolving time goes by, the film of resin drops off completely.

From the effect of inhibitational/accelerational matter and infrared dye on the resin, we find that the influence of the two is greatly significant than the single one. It lies in the degree of cross liking is larger in inhibitational/accelerational matter, infrared dye and resin than the single one.

Conclusion

Through the test of the alkaliresistance of the resorcinol resin and mix phenolic resin, we can find that the alkaliresistance of mix phenolic resin is larger than resorcinol resin. The influence of the single component of the inhibitational/accelerational matter or infrared dyes on the mix phenolic resin is larger than resorcinol resin. The influence of the two components of the inhibitational/accelerational matter and infrared dyes on the mix phenolic resin is obviously larger than resorcinol resin. Meanwhile, when the two components join together, the alkaliresistance is larger than the single component. The alkaliresistance of the mix phenolic resin can meet the requirement of plate development.

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Weimin Zhang, male, professor, graduated in East China University of Science & Technology in 1986. He is working in Lab. Printing & Packaging Material and Technology (Beijing area major laboratory), in Beijing Institute of Graphic Communication. His work is focused on organic information recording materials, especially organic photoreceptor, functional materials.

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