DYNAMICS AND RHEOLOGY OF INKS INCLUDING VARIOUS TYPES OF GELLING AGENTS

Takeshi Amari*, Wei Xianfu*, Tsutomu Hayashi**, and Kotaro Morita**

KeyWords: Rheology, Resin, Inks, Filament Length, Tack

ABSTRACT

In order to clarify the relation between the gelled structure in varnish, rheological proprties and printability, dynamics and rheological properties were examined for two kinds of varnishes which are prepared by chemically gelled binder and physical one.
Rheological properties such as dynamic viscoelastic properties and flow properties were measured using cone and plate rheometer. Dynamic behavior of liquid film splitting between rollers were investigated using a video monitoring and an acoustic techniques. The rheological properties of varnish are affected by density of structural networks. The network structure formed by the chelate type gellants is durable and stable under large deformation, therefore, the steady shear viscosity and normal stress of the vanish are extremely large in higher shear region. The varnish having chemically closs-linked bonding shows the large tack value and the longer filamentation. However, the varnish having physically closs-linked networks show the small tack value and the short filament, even though the denser network structure exists initially.
The remarkable difference between the varnish having chemically closs-linked bonding and that having physically closs-linked one was observed in the acoustic spectrum .

INTRODUCTION

In high speed lithographic offset printing, a lower tack level, a more stable rheological properties, a fast recovery of the structure are required for ink properties. The rheological properties of printing inks are affected by various factors, especially viscoelastic properties of resins in vehicle govern the rheological properties of the printing ink. At high

*Department of Image Science, Faculty of Engineering, Chiba University, 1-33 Yayouicho, Inage-ku, Chiba 263, JAPAN
** Sakata INX Co.,2291 Makinouchi, Ozaki, Noda-shi, Chiba 270-02, Japan

press speed, ink can damage the paper by causing picking. Picking can be avoided using stronger paper, lower press speed, or lower ink tack. In most cases, the paper cannot be changed, and a reduction in press speed is time consuming, therefore it is the best way to reduce ink tack. However, low viscous ink lead to misting and poor ink transfer. Then we have to choose appropriate resin to get good printability. It is said that the resin having gelled structure reduce the ink tack and improve printability (Kees, 1989).

In order to investigate the role of resins having gelled structure in the rheological properties and printability of inks, we measured the rheological properties of the varnish at first and observed dynamic behavior of the varnish on rotating rollers using video monitoring and acoustic techniques. Our goal is to clarify the relation between the gelled structure in varnish, rheological properties and printability. In this study we used the two kinds of varnishes prepared by rosin-based modified phenolic resin which provide difference types of gelled structure. One is chemically gelled binder and the other is physically one.

EXPERIMENTAL

Sample

Table 1 shows the composition of varnishes studied here.

Table 1

COMPOSITION OF SAMPLE VANISHES

	Normal Resin		Structured Hard Resin	
	#1 Vanish	#2 Vanish	#3 Varnish	#4 Vanish
Resin (%)	39.0	30.0	36.0	36.0
Linseed Oil (%)	23.0	23.0	21.0	21.0
Solvent (%)	37.7	37.5	43.0	43.0
Gellants (%)	0.3	0.5	-	-
Cooking Temp.(°C)	200	200	200	220

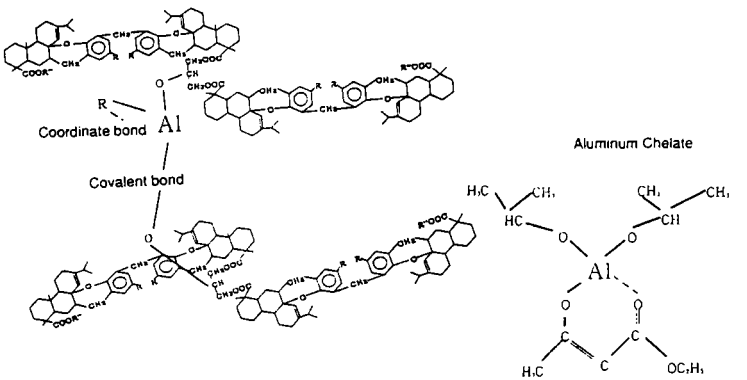

Figure 1. Structure of the Normal resin

In the varnishes #1 and #2, gelled structure was provided by ordinary way, that is, Aluminum chelate (AlCH) was added in the rosin modified phenolic resin. It is said that the chelate type of gellants form an "internal" gel which is not easily ruptured by heat. Networks are formed by covalent and coordination bonds, therefore the structural networks are thought to be durable and stable under large deformation. The density of polymeric networks depends on the amount of the gelling agent, then the denser network structure is predicted in #2 varnish. The structure of this type gelled resin is shown in Figure 1. We refer this type resin as "Normal resin".
#3 and #4 varnishes are made by rosin -based modified phenolic resin with many functional group and called "Structured hard resins". The functional hard resins form highly branched polymeric chains. The gelled structure was provide physically by semi crystallite domain and entanglements of branched polymeric chains without gelling agent such as AlCH. The structured hard resin studied here is a partly crystalline polymer. In the course of cooking the crystalline areas are gradually diminished and the distance between the polymer chain becomes wider with increasing temperature. Whole conformation of resin may be sphere swollen by medium oil and expands with rising the temperature. The network polymer chains penetrate and entangled each other and physically gelled structures are formed in the whole system. Network density depends on the distance between polymer chain and residual semi-crystalline phase. At lower cooking temperature, the denser network structure is expected.

Measurements

Rheological Properties

Measurements of dynamic viscoelastic properties were carried out using Rheometrics Fluid Spectrometer (RFS-II) with a cone and plate geometry. Storage and loss moduli, G' and G" were measured at the strain amplitude of 1% in the frequency region between 0.05 and 80 rad/sec. The measurements of the normal and shear stress in a shear field are performed at the rates of shear ranging from 10^{-2} to10^{2} sec^{-1} using Rheometrics Dynamic Analyzer (RDA-II). All the measurements were carried out at the temperature of 25 °C.

Splitting of liquid film between rollers

The growth of filaments between rollers was observed using a pair of disk rollers as shown in Figure 2. The video system consists of a microscope, a CCD video camera, and a personal computer with an image-processing board (Photoron FDM 98-4). The image of ink filaments can be analyzed every 1/60 sec. From the image analysis, the mean value and the standard deviation of the maximum filament length are determined.

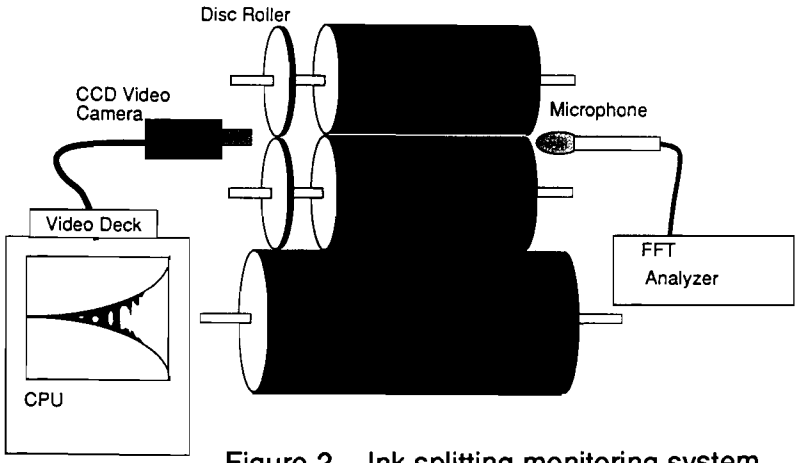

Figure 2. Ink splitting monitoring system

Acoustic noise may be related to rupture of materials. When ink film splits, high frequency noise may be generated. The acoustic study of the varnish film splitting was performed using a sound analyzing system which consists of a microphone with high sensitivity in the frequency region up to 50 kHz, and FFT analyzer.
Tackiness of varnish was measured at various roller speeds using the ordinary inkometer, developed by Reed.

RESULTS

Dynamic Viscoelastic Properties

Figures 3 and 4 show the frequency dependence of G' and G", respectively, for various varnishes. The values of G' and G" increase with increasing angular frequency. The magnitude of G' and G" for varnish #3 is the largest of all. In the lower frequency region, the values of G' and G" for the varnishes consisting of the structured hard resin seem to be larger than those of normal resin. We can deduce the network density of the system from G' and G" in lower frequency region, because of the network structure behaves as relaxation mechanisms with longer relaxation time.

Apparent Viscosity and Normal Stress in Steady Shear Flow

Figure 5 shows logarithmic plots of apparent viscosity against rate of shear for various varnishes. In lower shear rate region, the values of viscosity seem to be constant irrespective of rate of shear. Equilibrium value of viscosity depends on the degree of gelation. However, in higher shear region above 10 s^{-1} the values of viscosity decrease with increasing rate of shear, this tendency is remarkable in the varnishes consisting of the structured hard resin.

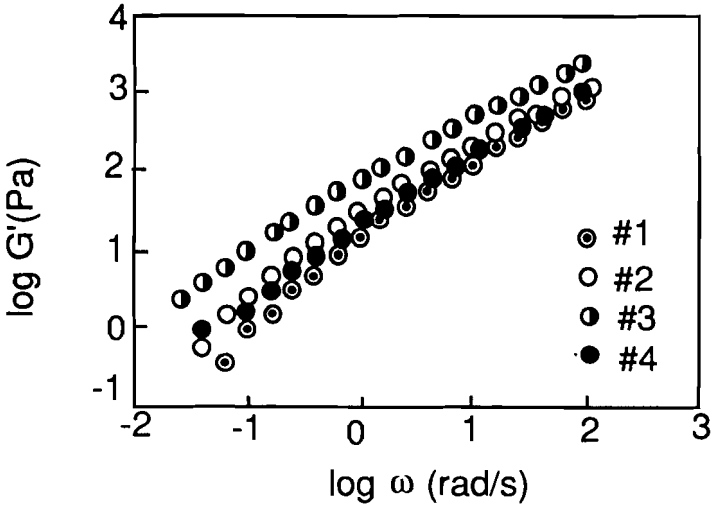

Figure 3. Frequency dependence of storage modulus for various vanishes.

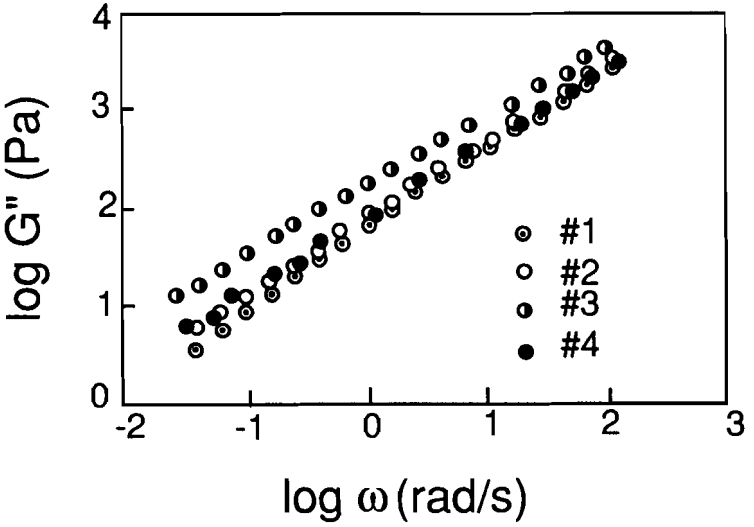

Figure 4. Frequency dependence of loss modulus for various vanishes.

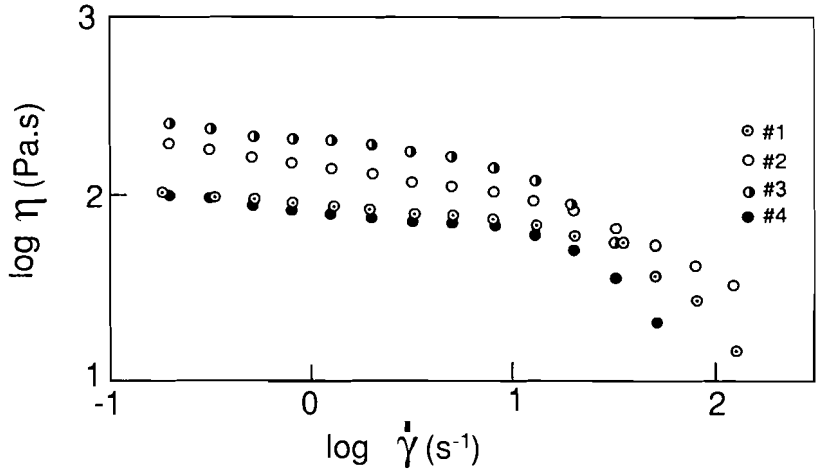

Figure 5. Logarithmic plots of apparent viscosity against rate of shear for various vanishes.

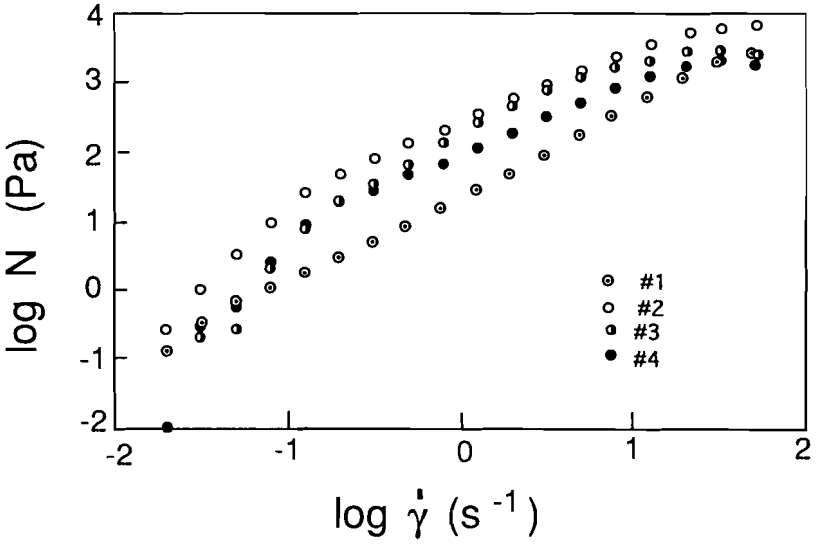

Figure 6. Logarithmic plots of normal stress against rate of shear for various vanishes.

Figure 6 shows logarithmic plots of normal stress, N1 against rate of shear for various varnishes. The values of N1 for #1 varnish are larger than those for other varnishes in whole shear rate region. In higher shear region the values for #3 and #4 varnishes decrease with rate of shear. The value of N1 and its shear rate dependence are determined by molecular weight of polymeric chains and intermolecular interactions.

Temperature Dependence of Steady State Viscosity

Temperature,T dependence of steady state viscosity, η were measured at 0.1 sec^{-1}. The plots of ln η against 1/T are shown in Figure 7. With decreasing temperature, the temperature dependence of η becomes pronounced and this tendency is distinguish in the varnish of the structured hard resin. The activation energy for viscous flow can be calculated from the linear portion of the plots. The values of the activation energy at lower temperature for varnishes of the normal resin and the structured hard resin are 5.7 kJ and 7.8 kJ, respectively.

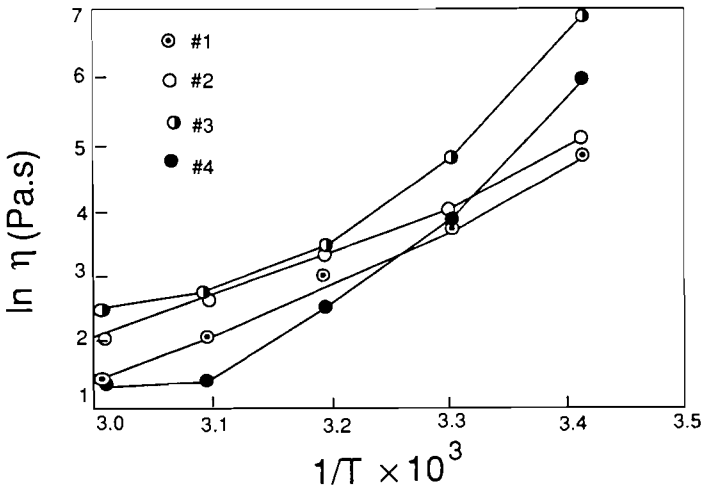

Figure 7. The relation between apparent viscosity and temperature for various vanishes.

Tackiness

Tackiness of varnish was measured as a function of elapsed time. The results are shown in Figure 8. Tack value for the varnish of the structured hard resin is smaller than that of the normal resin and the tack value for the varnish of the normal resin increases with elapsed time. This phenomenon can be explained by evaporation of solvent and volatile diluent in the varnish.

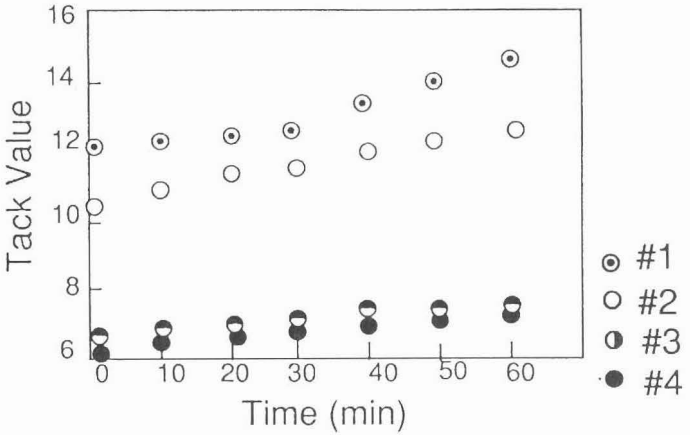

Figure 8. Time dependence of tack value for various vanishes.

Visual Examination of Film Splitting

The splitting of liquid film of varnish between rollers can be analyzed visually using the video system.

Figure 9 shows one frame of video recording microscopic image at the nip exit of rotating disks. The picture was taken by CCD video camera every 1/60 sec with the aid of a high speed electronics shutter in an exposure time of 1/5000 sec. It was observed that the filaments

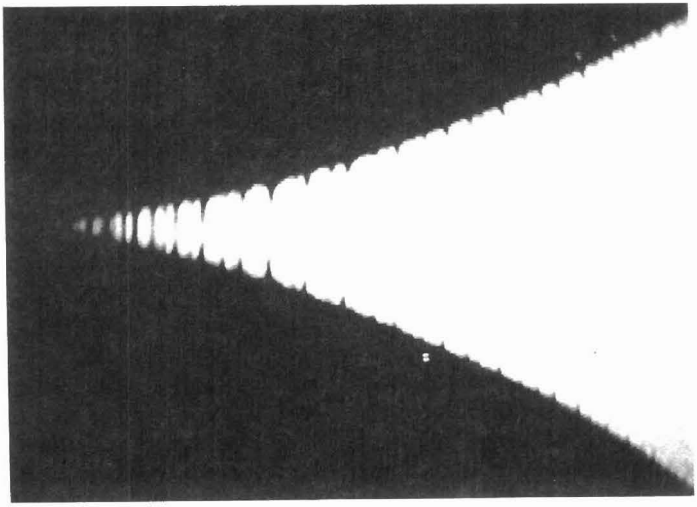

Figure 9. Picture of video recording microscopic image at the nip exit of rotating disks.

reached a maximum length of about 30 - 200 times of the original film thickness before rupturing. If an ink filament is elongated slowly, a ductile failure and a viscous flow may occur. However, as the speed of splitting becomes higher, the filaments are ruptured as elastic materials and are quickly retracted to the roller surface. Then, at a higher rate of separation, a shorter ink filament is observed at the rupturing point.

Figure 10 shows the plots of the average filament length against elapsed time for various varnishes at the rotating speed of 100 rpm. For varnishes consisting of the normal resin, the filament length is high at initial stage but decreases with increasing elapsed time, however, for varnishes consisting of the structured hard resin, the filament length is comparatively short, but the length seems to be constant irrespective of time.

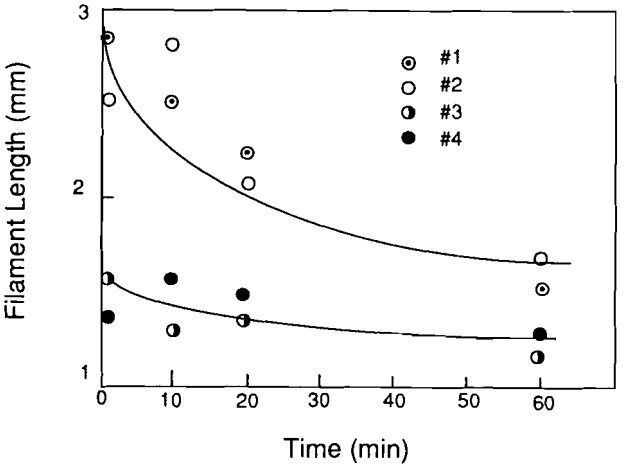

Figure 10. The plots of the average filament length against elapsed time for various varnishes at the rotating speed of 100 rpm.

Acoustic Measurement

Filament splitting sound of liquid varnish film between roller nip were evaluated by an acoustic spectrum. We defined the acoustic spectrum as the power density of the sound at the corresponding frequency. Figure 11 shows the acoustic spectrum for various varnishes. Rotating speed of rollers was 400 rpm. The effect of inherent sound owing to roller rotating is subtracted from the spectrum in advance. The splitting sound of liquid film affects the power density of the spectrum in the frequency region between 10 to 40 kHz. Higher and broader peak is observed at 20 kHz in the spectrum for the varnishes consisting of the structured hard resin.

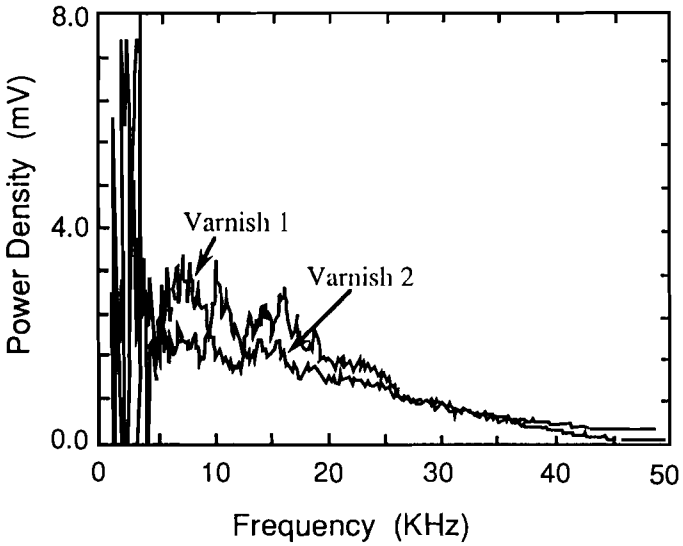

Figure 11(a). The acoustic spectrum for #1 and #2 varnishes. Rotating speed of rollers was 400 rpm.

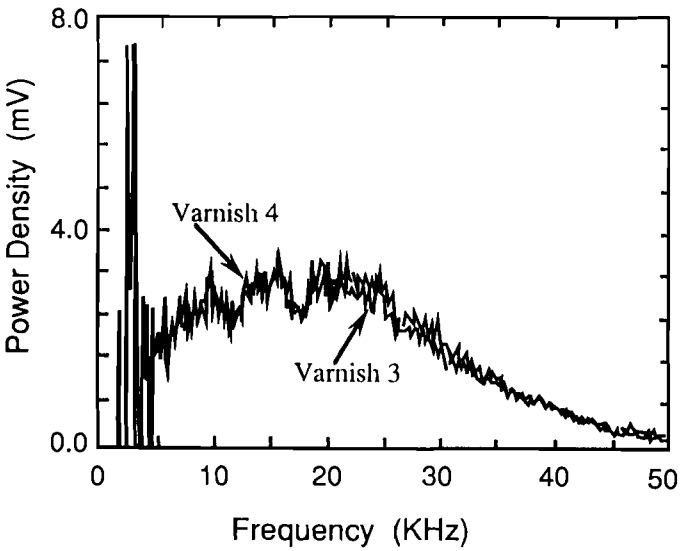

Figure 11(b). The acoustic spectrum for #1 and #2 varnishes. Rotating speed of rollers was 400 rpm.

On the other hand, for the varnishes consisting of the normal resin, high frequency components are reduced and the peak shifts to lower frequency. The peak value becomes smaller with increasing viscoelasticity of the system.

Figure 12 shows plots of the power density at 20 kHz against elapse time for #1 and #4 varnishes and the values decease with increasing time. For the varnish consisting of the structured hard resin, the values of the power density are comparatively high and the time dependence is remarkable.

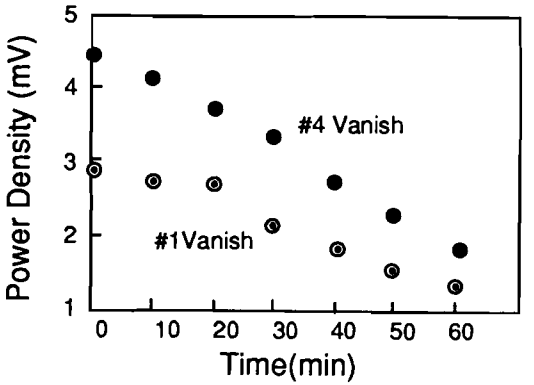

Figure 12. Plots of the power density at 20 kHz against elapse time for #1 and #4 varnishes

DISCUSSION

Rheological Properties and Structure of Gel Varnish

A polymer gel has a network structure, whether linked by chemical bonds or crystallite or some other kind of temporary junction. In a concentrated polymer solution, long-range configurational changes of polymer chain, including the slippage or dissociation of entanglements take place at lower rate of shear and their behavior seems to be responsible for relaxation mechanisms with longer relaxation time in dynamic measurements.

In the dynamic measurement, the relaxation mechanisms with longer relaxation times govern the viscoelastic characteristics in the lower frequency region. In lower frequency region, so called the "terminal flow region", G' increases in proportion to the square of frequency for the Maxwell type relaxation system. If chemical cross-links are introduced to serve as permanent network junctures, the terminal flow region is suppressed and the frequency dependence of G' and G" in lower frequency region becomes smaller. We can deduce the density of structural networks from the frequency dependence of viscoelastic functions in the lower frequency region (Ferry, 1978).

In the varnishes #1 and #2, networks are formed by covalent and coordination bonds, therefore the structural networks are thought to be durable and stable under large deformation. On the other hand, in the varnishes #3 and #4, the gelled structure is formed physically and network density depends on the cooking temperature. The lower cooking temperature, the denser networks are constructed

The values of G' and G" of varnish #3 are larger than those of other varnishes in the whole frequency region. In #3 varnish, physical entanglements and semi-crystalline phase behave as temporally closs linked junctions, therefore, the density of structural networks formed by the structured hard resin prepared at lower cooking temperature may be the highest of all. The density of network structure also affects the flow properties at comparatively lower rate of shear. In the plots of the apparent viscosity against rate of shear (Figure 5), the values for #3 varnish are larger than the others, however, the value decreases rapidly with increasing rate of shear in higher shear rate region.

On the other hand, for varnishes consisting of the normal resin the viscosity does not depend so much on rate of shear and comparatively higher viscosity is observed at the shear rate over 100 sec^{-1}. The values of normal stress for #2 varnish is the largest of all. From the results of steady shear experiments, it is expected that the molecular weight of polymeric chain consisting of the normal resin with large amounts of gellant is extremely high and the closs-links formed by the chelate type gellants are not easily raptured under higher shear rate.

However, for the physically gelled resin the structured networks may be raptured under higher shear rate even though the denser network structure exists initially. They behave as typical thixotropic materials. In the varnishes consisting of the structured hard resin, the network structure and its kinetic property are extremely affected by external force and temperature. In the physically constructing network structure, the forces exerted on the network chain may be increased with proceeding contraction of the gelled structure. Therefor, in #3 and #4 varnishes the viscosity increases drastically with decreasing temperature, in contrast to the ordinary temperature dependence of viscosity is observed in #1 and #2 varnishes.

Printability and Rheological properties

Splitting behavior of liquid film must be associated with the rheological properties of the liquid. Tackiness, filamentation and shortness of printing inks can be predicted by the rheological properties.

Figure 8 shows the tack values of varnishes consisting of the normal resin are extremely larger than those of the structured hard resin. It is very interesting that tack values of #3 varnish are smaller than those of #1 varnish, whereas in #3 varnishes larger values of G',G", and apparent viscosity are observed at lower frequency or lower rate of shear.

Voet and Geffken (1951) pointed out that tack is the resistance of the ink to separation and is determined by the viscoelastic response of the inks toward rapid applied stress. Myers and co-worker(1959) defined that tack is "The splitting of thin liquid films involves an elusive quality of stickiness or adhesiveness which may or may not be a unique physical properties of the material being split". Zang and co-workers (1991) defined ink tack to be the maximum tensile stress that the ink can withstand at the nip exit. Generally it is thought that tackiness is the resistance offered by liquid films during splitting where the process proceeds at the time scale of the order of 0.01 sec or shorter. Then the small tack value for the varnish consisting of the structured hard resin can be predicted by the remarkable shear shinning behavior at higher shear rate.

During film splitting in the varnish consisting of the normal resin, the length of filament is comparatively long initially, however the length decreases with elapsed time as shown in Figure 10 . This phenomenon seems to be associated with evaporation of solvent or lower molecular weight components and corresponds to the dependence of tack value on elapsed time, in other word, the rigidity of the varnish increases with time. In the varnish consisting of structured hard resin, the initial length of filaments is not so long, then the dependence of length on time is not clear, they seem to be constant irrespective of time. Shorter length of filament is closely associated in the flow properties, that is, characteristics of the plastic flow are observed obviously in the varnish consisting of structured hard resin.

These results may be attributed to the difference in network structures, namely, the closs-linked coupling in the network structure formed by the normal resin is provided by covalent and coordination bonds, in contrast to the network structure formed by the structured hard resin is provided by the temporally physical bonding. The network structure of the normal resin is comparatively durable and stable under large deformation, however, that of the structured hard resin may be easily dissociated with applying larger deformation. The large values of normal stress and the higher filamentation in #2 varnish can be attributed to the extremely large molecular weight of the polymeric chains.

Film splitting behavior on rotating rollers can be investigated with the acoustic spectrum.We have reported that the power density in the acoustic spectrum decreases with proceeding emulsifying water in ink in offset lithography (Hayashi and Amari, 1992). Although precise relation ship between rheological properties and acoustic properties has not been clear, it is interesting that a marked difference in the acoustic spectrum exists between the varnish containing of the normal resin and that of the structured hard resin.

CONCLUSIONS

Rheological experiments are performed for two kinds of varnishes which are prepared by chemically gelled binder and physically one. The relations between rheological properties and film splitting behavior are mainly discussed by considering the change in gelled structure. And following conclusions are obtained.

1.The varnish having physically forming denser network structure shows a shear thinning behavior attributable to rupturing the temporary closs-linked junctions.

2. The network structure formed by the chelate type gellants is durable and stable under large deformation, therefore, the steady shear viscosity and normal stress of the vanish are extremely large in higher shear region.

3. The varnish having chemically closs-linked bonding shows the large tack value and the longer filamentation. However, the varnish having physically closs-linked networks show the small tack value and the short filament, even though the denser network structure exists initially.

4. The remarkable difference between the varnish having chemically closs-linked bonding and that having physically closs-linked one was observed in the acoustic spectrum .

Literature Cited

Ferry J.D.
1980 " Viscoelastic Propertie of Polymers", (John Wiley & Sons Inc.) , 3rd. ed.

Hayashi T. and Amari T.
1992 "Dynamics of Transfer and Splitting of Emulsified Ink", International Printing & Graphic Arts Conference, 75-80

Kees van Esch
1989 "These Studies Show That Gelation Can Be effective in Reducting Tack in Web Offset Inks", American Ink Maker / Feburuary, 28-33

Myers R.R., Miller J.C., and Zettlemoyer A.C.
1959 "The Splitting of Thin Liquid Films. Kinematics" J. Colloid Sci., vol. 14, 287-299

Voet A. and Gafken C.F.
1951 "The Nature of Tack" Industrial and Engineering Chemistry, vol. 43, 1614-1623

Zang Y.H., Aspler J.S., Boulk M.Y., and DeGrace J.H.
1991 "Direct Measurement of tensile Stress ("Tack") in Thin InkFilm" J. Rheol., vol 35, 345-361