Semi-Transparent Optical Coating for Security Holograms

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ABSTRACT

Holography has become a rapidly growing, global industry to protect products and documents against counterfeiting and tampering. Today, there are so many types of holograms to choose from for particular application. The need to protect some of the security document features by an overlay, led to the development of see-through diffractive optically variable image device, or DOVID, holograms. Rapid advances in DOVID holograms led to a growing requirement for high refractive index (HRI) coatings to enhance reflectance while maintaining high transparency. Among HRI materials gaining growing interest for such applications is Zinc Sulphide.
In the present investigation, a plasma source was incorporated to treat the base-coated PET film surface prior to deposition of ZnS. This paper reviews the results of utilizing plasma treatment to deposit high quality ZnS coating on a moving web for security holograms.

INTRODUCTION

Over the past few years holograms have grown into a complex business to prevent counterfeiting of security cards, banknote and security labels [1,2]. The rapid advances in holographic technology have led to the development of see-through diffractive optically variable image device, or DOVID, holograms [3]. The surface relief pattern of the DOVID is embossed into a clear base coat, which is applied onto a polyester substrate. The pattern is then covered with a high refractive index (HRI) coating so that the incident light is still diffracted and the image is bright. The advantage is that when the DOVID is applied to a security document, for example over a photograph, no direct optical copy can be made of the DOVID without copying all the individual data at the same time. Among HRI materials gaining growing interest for such an application is Zinc Sulphide. For holographic applications, HRI coatings have to fulfill certain requirements such as easy to detect colour shift, high transparency for see through applications, repeatability and consistency, compatibility to document structure, durability, stability and low cost. Zinc sulphide can meet most of such stringent requirements [4]. Adhesion of ZnS on base-coated PET film is one of the most important factors to achieve high reflectance and good uniformity. In the present investigation, a plasma source was incorporated to treat the base-coated PET film surface prior to deposition of ZnS. This paper reviews the results of utilizing plasma treatment to deposit high quality ZnS coating on a moving web for security holograms. The optical and structural characteristics of ZnS were examined using optical spectrometry and atomic force microscopy. Coatings with 35-40% reflection in the visible region were achieved.

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EXPERIMENTAL WORK

The present work was carried out inside a 2m diameter, two zones vacuum roll coater. The vacuum chamber contained unwinding/rewinding drives, water-cooled drum, plasma source and a thermal evaporation source. The plasma treatment source consisted of AC powered, magnetically enhanced dual electrodes with one racetrack per electrode. The source was enclosed in a pressure-controlled zone to maintain stable plasma. Zone sealed rollers were used for web control in the plasma zone. A closed loop circuit controlled the gas flow to the plasma source. The source was operating at 40kHz, 5kW power and used a gas mixture of 80% argon and 20% oxygen for treatment. Figure 1 shows a schematic diagram for the experimental setup.

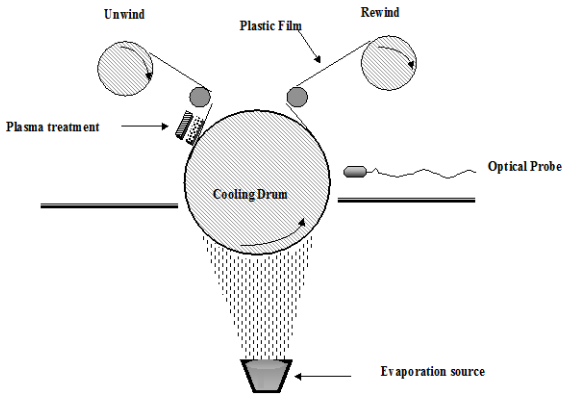

Figure 1. Schematic diagram of the roll coater

The chamber was pumped down directly by rotary and diffusion pumps to a base pressure of $5x10^{-5}$ mb. During operation of plasma source the pressure in the plasma unit was $5x10^{-2}$mb. However, plasma treatment did not affect the pressure in the coating zone. For the deposition of zinc sulphide coating onto a moving polyester film, ZnS granules from Merck were used. On-line monitoring of coating reflectance was carried out using Ocean Optics SQ2000 optical spectrometer in the visible region. During coating, the base-coated polyester film was treated with the Ar/O_2 plasma before entering coating zone. Coating thickness was controlled to give a high reflectance in the visible region as monitored by on-line spectrometer. Coating thickness and uniformity was controlled by evaporation source power, line speed and power on plasma source. The final spectral transmittance and reflectance were measured using a Perkins- Elmer Lambda 9 spectrophotometer. Atomic Force Microscopy (AFM) was used to determine coating structure, roughness, grain size and defect morphology. X-ray analysis was carried out using Electron Depressive Spectroscopy (EDS) on a LEICA S430 Scanning Electron Microscope. Table 1 summarises the deposition parameters used in this work.

Table I
Deposition parameters of ZnS coatings onto base- coated PET film

Process Parameters	Typical Values
Type of Film	12-50μ PET
Film width	600-1600mm
Pressure in coating zone	$4x10^{-4}$mb
Line speed	200m/min
Coating thickness	450-550Å
Coating uniformity	± 5%
Starting material	ZnS granules
Refractive index	>2.2
Absorption	<2.8%
Reflectance	35-40%
Coating tone	light yellow
Adhesion	Excellent
Film length	3000-5000m

RESULTS AND DISCUSSION

ZnS coatings were deposited onto 12 μ base-coated polyester films at line speeds from 60-200m/min. Different types of PET/base-coat combinations were tested to evaluate their compatibility with ZnS coating. Plasma treatment was utilized to improve the adhesion of ZnS coating onto base-coated PET films. For comparison, some films were prepared without plasma treatment. In the present work it was found that plasma treatment would be necessary to enhance the sticking coefficient of ZnS on some types of base-coats particularly those with high water or solvent contents. Fig. 2 shows the increase in ZnS coating thickness onto 12μ base-coated PET film following plasma treatment. Without plasma treatment, it was only possible to deposit ZnS at a line speed of 60m/min. At a line speed >60m/min, ZnS would not stick onto some types of base-coats without plasma treatment. It is possible to suggest that such base-coats were either not fully cured or it could have retained solvent or water due to in-adequate drying during lacquering stage. Any retained solvent/water would be released in the coating zone to prevent adhesion. However, following plasma treatment at 5kW the adhesion of ZnS improved drastically and the coating was deposited at a line speed >60m/min as shown in Fig. 2.

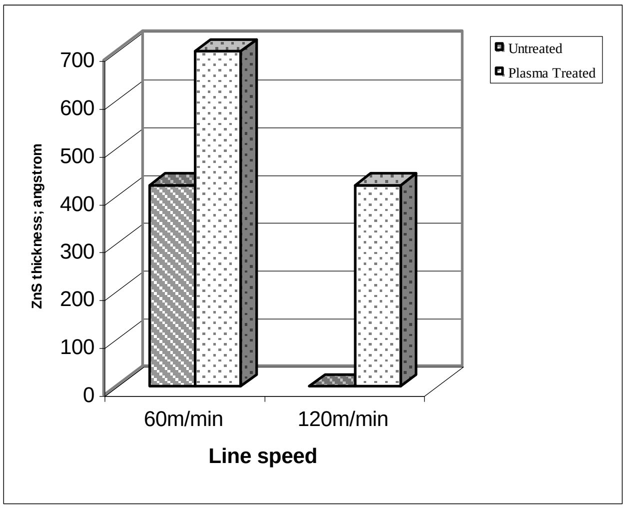

Fig. 2. Effect of plasma treatment at 5kW power on adhesion of ZnS onto a 12μ base-coated PET film

The surfaces of films coated with ZnS were examined by AFM. The analysis shows that the surface morphology depends on substrate treatment prior to depositing ZnS. In general, the surface roughness and grain size of ZnS coating decreases following plasma treatment of base-coated PET films as shown in figures 3 and 4. Films treated with plasma prior to depositing ZnS have a smoother surface and a smaller grain size. Ion bombardment during coating deposition is known to densify the structure and improves adhesion. In the present work, however, plasma treatment of base-coated PET was carried out before depositing ZnS. This means that ion bombardment with gases containing oxygen has dried and smoothened the surface of base-coat and subsequently increased surface energy. The increase in surface energy enhances the adhesion of ZnS onto base coat [5,6].

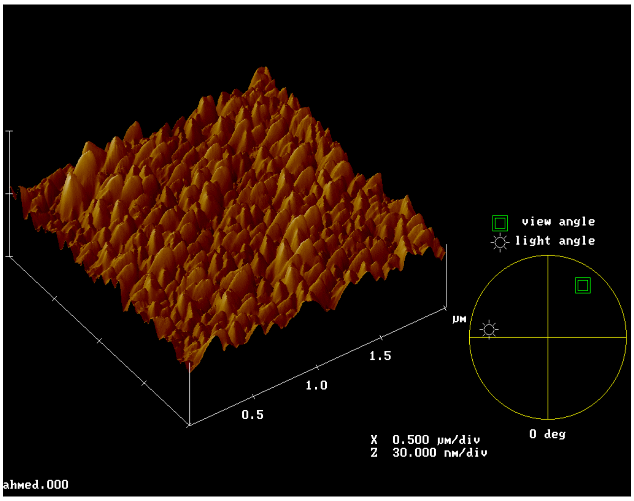

Fig. 3. AFM image of 450Å thick ZnS onto untreated 12µ base-coated PET film

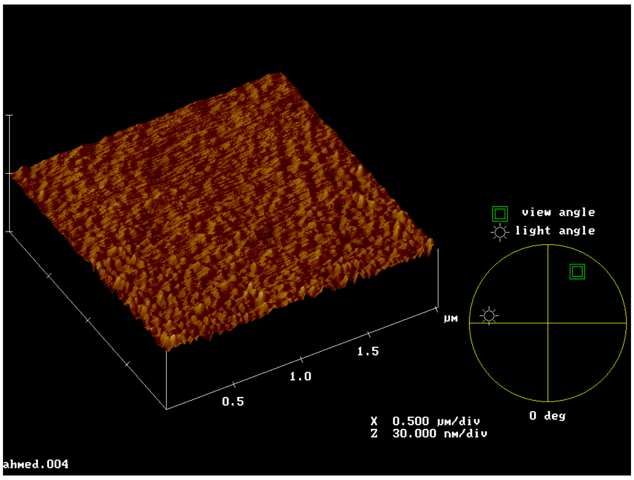

Fig. 4. AFM image of 450Å thick ZnS onto plasma treated 12 µ base-coated PET film

Figures 3 and 4 also show that the surface morphology of ZnS coating changes from coarse columnar structure with a grain size of approximately 160nm without a plasma treatment of base-coat, to a fine structure with small grains of approximately 40nm in size following plasma treatment of base-coat. The above result indicates that the growth of ZnS coating is influenced by the physical and chemical state of base-coat applied onto PET films. Therefore, any defect in the base-coat would have an influence on the final optical quality of ZnS coating. In the present investigation a tree-like effect was observed on some type of base-coats following deposition of ZnS. The increase in surface reflectance following deposition of ZnS enhances this effect. The tree-like defect can be caused by electrostatic discharge either during lacquering stage in air or near the parting line at web payout from the roll in vacuum [7]. When present, tree-like defects are cause for immediate rejection since it would affect the optical properties of the embossed holographic image. However, the use of plasma treatment prior to depositing ZnS reduces this problem probably by neutralizing charge build up on the substrate surface. An x-ray analysis was carried out to investigate the presence of any possible contamination in the ZnS deposited coating. Figure 5 show the result of the x-ray analysis of 450 Å thick ZnS coating onto plasma treated 12µ base-coated PET film. The figure exhibits clearly the Zn and S peaks and shows that the content of sulphre is higher than expected. Calculation based on this analysis indicates that the ZnS coating has 57.7% by weight Zn and 42.3% by weight S. The Al peak is due to the aluminium substrate holder used in the analysis. The Cl peak is due to the chlorine in the base-coat or PET film. No other contaminants are observed in the analysis. Measurement of refractive index using ellipsometry shows that this coating has a refractive index of 2.35. The absorption of the deposited ZnS coating was measured from the transmittance and reflectance data

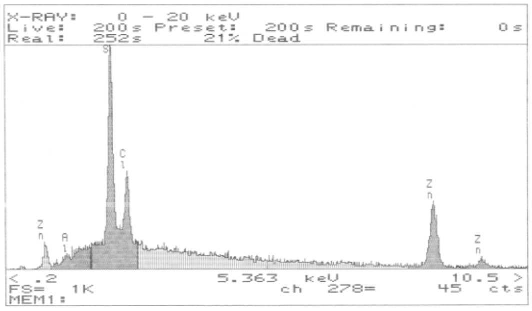

Fig. 5. X-ray analysis of 450Å thick ZnS coating onto plasma treated base-coated 12µ PET film

and found to be less than 2.8%. Figure 6 shows a typical reflectance graph of plasma treated 12µ base-coated PET film. The figure shows clearly that reflectance at 550nm wavelength increases from 13% for uncoated film to 40% for ZnS coated film.

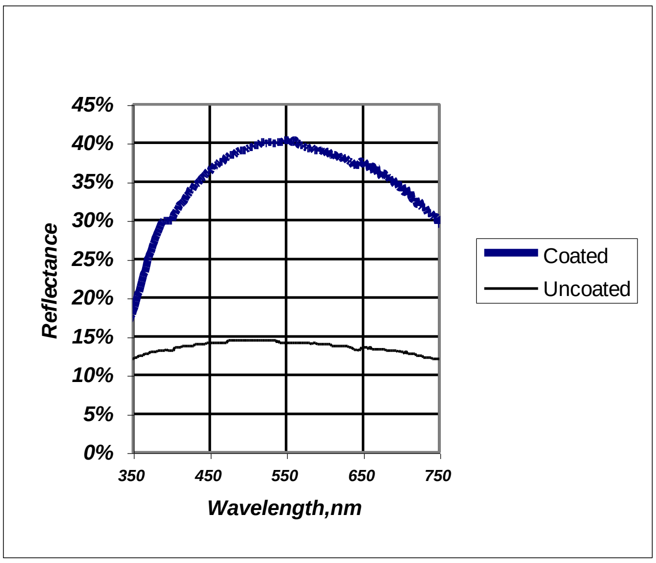

Figure 6. Reflectance of ZnS onto plasma treated 12 μ base-coated PET film at a line speed of 200m/min

The uniformity of ZnS coating across film width was measured. The coating was deposited at a line speed of 200m/min. Figure 7 shows the coating uniformity across the width of 1300mm wide, plasma treated 12μ base-coated PET film. The measured uniformity is ±5% across the width.

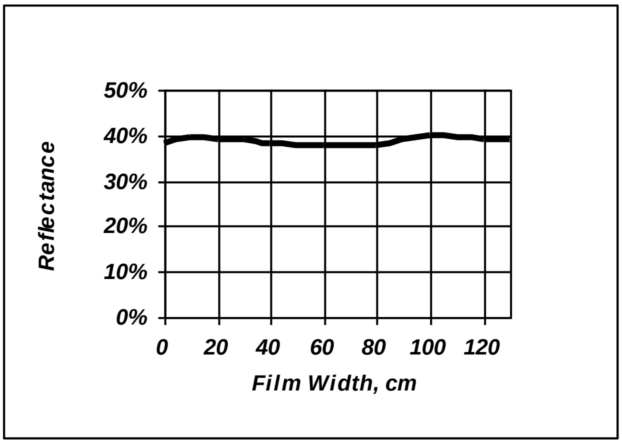

Figure 7. Uniformity of ZnS across 1300mm wide, plasma treated 12μ base-coated PET film at a line speed of 200m/min

CONCLUSIONS

Our investigations have shown that plasma treatment of base-coated PET film prior to depositing ZnS has a considerable influence on the coating properties. Without plasma treatment, it was difficult to deposit a uniform ZnS coating on some types of base-coated PET films at a line speed of more than 60m/min. The coating structure was columnar with large grains. Coatings obtained with a plasma treatment have a fine structure with small grains and a high refractive index with absorption level of less than 2.8%. Plasma treatment also enhances the adhesion of ZnS coating on base-coated PET film. Therefore, the coating can be deposited at a line speed of 200m/min. The coating uniformity across film width is better than ±5%. All coatings have a low level of stress and are highly adherent to the substrate. The process is now used to produce high quality holograms for security applications.

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