PROCEEDINGS

Polymers, Laminations and Coatings Conference

Book 2

TAPPI PROCEEDINGS

Polymers, Laminations and Coatings Conference

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Book 2

TAPPI PRESS

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TAPPI is a professional and scientific association organized to further the application of science, engineering, and technology in the pulp and paper, packaging and converting, and allied industries. Its aim is to promote research and education, and to arrange for the collection, dissemination and interchange of technical concepts and information in fields of interest to its members. TAPPI is not intended to, and may not, play any role in the competitive decisions of its members or their employers, or in any way restrict competition among companies.

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In addition to the Association's firm commitment to the principle of competition served by the antitrust laws, the penalties which may be imposed upon both the Association and its individual and corporate members involved in any violation of the antitrust laws are so severe that good business judgment demands that every effort be made to avoid any such violation. Certain violations of the Sherman Act, such as price-fixing, are felony crimes for which individuals may be imprisoned for up to three (3) years or fined up to \$100,000, or both, and corporations can be fined up to \$1 million for each offense. In addition, treble damage claims by private parties (including class actions) for antitrust violations are extremely expensive to litigate and can result in judgments of a magnitude which could destroy the Association and seriously affect the financial interests of its members.

It shall be the responsibility of every member of TAPPI to be guided by TAPPI's policy of strict compliance with the antitrust laws in all TAPPI activities. It shall be the special responsibility of committee chairmen, Association officers, and officers of Local Sections to ensure that this policy is known and adhered to in the course of activities pursued under their leadership.

To assist the TAPPI staff and all its officers, directors, committee chairmen, and Local Sections officers in respectiving

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The following rules are applicable to all TAPPI activities and must be observed in all situations and under all circumstances without exception or qualification other than those noted below:

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 b. reducing competition in the marketplace with
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9. No TAPPI activity or communication shall include any

discussion which might be construed as an attempt to prevent any person or business entity from gaining access to any market or customer for goods or services, or to prevent any business entity from obtaining a supply of goods or otherwise purchasing goods or

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12. No TAPPI activity or communication shall include any discussion which might be construed as an agreement or understanding to refrain from purchasing any raw material, equipment, services or other supplies from any supplier.

13. Committee chairmen shall prepare meeting agendas in advance and forward the agendas to TAPPI headquarters for review prior to their meetings. Minutes of such meetings shall not be distributed until they are reviewed for antitrust implications by

TAPPI headquarters staff.

14. All members are expected to comply with these guidelines and TAPPI's antitrust policy in informal discussions at the site of a TAPPI meeting, but beyond the control of its chairman, as well as in formal TAPPI activities.

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TAPPI headquarters needs to remain aware of what particular committees and sections of TAPPI are doing or planning to do in committees and sections of TAPPI are doing or planning to do in order to better assist those groups in achieving their objectives and to continue to supervise actively the antitrust compliance of TAPPI. The Board of Directors of TAPPI therefore has adopted this formal statement of TAPPI's policy which requires that persons corresponding or receiving correspondence on behalf of TAPPI provide copies of the type of correspondence outlined below to the appropriate liaison person at TAPPI headquarters.

For this policy TAPPI does not require copies of routine, written communications regarding arrangements for speakers, meetings, travel, dinner reservations and the like.

TAPPI headquarters does require that copies of

TAPPI headquarters does require that copies of correspondence of an important nature and of non-routine matters be supplied in a timely fashion to TAPPI headquarters personnel connected with the committee or section involved as shown below:

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- 2. Communications with other TAPPI committees or sections. 3. Communications with persons or organizations outside
- TAPPI. 4. All written or recurring verbal complaints or criticisms of TAPPI activities.

All correspondence falling under the above-stated policy must be forwarded promptly to the appropriate TAPPI headquarters liaison person, preferably at the time of transmittal or receipt.

SHORT CONTENTS

Session Number	Session Title/Page Number				
Book 1					
1	Management Panel: Packaging and Converting - Yesterday, Today, Tomorrow / 1				
2	Silicone Release Coatings Technology - Present and Future / 3				
3	Quality Control for Barrier Testing / 27				
4	Successful Compliance with Inks and Coatings - Panel Discussion / 35				
5	Film Extrusion Technology / 59				
6	Substrate Options for Packaging and Labelling I / 77				
7	Recent Equipment Advances for Flexible Packaging Applications / 93				
8	Substrate Options for Packaging and Labelling II / 119				
9	Pressure Sensitive Adhesives / 141				
10	10 Film Extrusion Equipment / 163				
11.	Differential Offset Gravure Precision Coating / 189				
Treating Techniques and Surface Effects in Extrusion Coating / 213					
13	3 UV/EB in the Converting Industry - An Update / 241				
14	Flexible Packaging: The End-User's Viewpoint - Panel Discussion / 27				
15	Pressure Sensitive Applications / 279				
16	Recycling and Disposal of High Barrier Packaging Materials / 291				
Book 2					
17	Treatment Required for Printing with Water Borne Inks / 333				
18	New Product Opportunities with UV/EB / 339				
19	Additives and Modifiers for Extrusion / 365				
20	Metallizing of Flexible Substrates I / 397				
21	Compliance Adhesives and Coatings / 433				
22	Rigid Barrier Containers Over the Next Decade - Panel Discussion / 461				
23	Statistical Quality Control I / 469				
24	Film Coextrusion Technology / 491				
25	Hot Melt Technology I / 527				
26	Metallizing of Flexible Substrates II / 557				
27	Statistical Quality Control II / 581				
28	Aqueous Adhesive and Coating Technology / 583				
29	Resins for Film Extrusion / 613				
30	Hot Molt Technology II / 653				

CONTENTS

Paper Number	Title/Page Number Author(s)				
17-1	Treatment Required for Printing with Water-Based Inks / 333 D. A. MARKGRAF				
17-2	Panel Discussion / 337 J. V. BENHAM				
18-1	UV Curing Systems: Basics to Recent Advances / 339 R. W. STOWE				
18-2	TEGO® Silicone Acrylates RC for Release Coatings / 343 C. WEITEMEYER, J. JACHMANN, D. ALLSTADT, and H. BRUS				
18-3	UV and EB Curable Laminating Adhesives / 355 S. M. ELLERSTEIN and S. A. LEE				
18-4	Formulation of UV and EB Coatings for Improved Performance and Profits / 361 J. P. GUARINO				
19-1	New Property Combinations Available with Mineral Reinforcement of Commodity Blown Films / 365 F. A. RUIZ and C. F. ALLEN				
19-2	Improvements in Polyolefin Blown Film Extrusion by Using a Novel Processing Aid / 375 P. A. SCHUMACHER and G. A. BREWER				
19-3	Adhesive Resins for Coextruded Barrier Structures / 383 M. W. POTTS				
19-4	New Extrudabale Adhesive Polymer For PVDC / 391 R. M. WARD and D. C. KELLEY				
20-1	Metallizing Equipment for Flexible Substrates / 397 E. K. HARTWIG				
20-2	The Latest in Board and Paper Metallization, An Easy Choice / 403 A. PASQUI				
20-3	Metallized Paper: Reflections on the Past, Designs on the Future / 415 W. RUFTY				
20-4	Industrial Applications for Metallized Flexible Substrates $$ / 421 J. W. COX				
20-5	Innovations in the Use of Metallized Polyester Film / 425 P. F. STECHER				
21-1	Graphic Arts Regulations / 433 A. WILSON				
21-2	Metering, Mixing and Dispensing 100% Solid Materials for Film Laminating / 435 K. A. JACOBS				
21-3	Commercial Compliant Adhesives / 447 R. BASHFORD				
21-4	Waterbased Materials - A Converter's Viewpoint / 453 R. C. PARSONS				
21-5	VOC Free Water Based Urethane Laminating Adhesives / 457				

22	Rigid Barrier Containers Over the Next Decade/Panel Discussion				
	New Generation of Plastics for Packaging Applications / 461 L. J. BONIS				
·	Rigid Barrier Containers Over the Next Decade / 463 R. E. FOSTER and S. STEFANOVIC				
	Innovations in High Barrier Materials and Structures / 467 J. MILTZ				
23-1	An Introduction to Statistical Process Control / 469 C. M. LANDEGGER				
23-2	Vendor Statistical Process Control - An Expanded View of Quality Requirements / 475 J. D. NEWMAN				
23-3	Customer Expectations/Vendor's Awareness — S.P./Q.C. / 479 G. R. RENSCH				
23-4	Statistical Process Control: An Overview of Goals and Implementation / 483 R. T. O'CONNELL				
24-1	Coextrusion: Mechanical and Practical Considerations in Blown Film Die Design / 491 P. C. GATES				
24-2	Feedblock Coextrusion Systems / 501 P. CLOEREN, JR.				
24-3	Practical Considerations in Barrier Film Coextrusion / 513 H. J. BRAX				
24-4	On-Line Layer Discrimination of Multi-Layer Structures / 519 S. I. SHAPIRO				
24-5	Development of Coextrusion Adhesives for Barrier Packaging / 523 T. T. CHIU, W. J. FAIRCHOK and B. P. THILL				
25-1	Priming for Hot Melt Adhesion / 527 F. M. SINGER and V. P. CUSHING				
25-2	Formulating to Enhance the Radiation Crosslinking of Thermoplastic Rubber for Hot Melt PSA's / 533 E. E. EWINS, JR. and J. R. ERICKSON				
25-3	Stabilization and Basic Understanding of Stabilizer Performance in SIS Based Pressure Sensitive Adhesives / 547 A. PATEL and R. THOMAS				
25-4	Tackifier to Modifier - Responding to Formulators' Needs / 553 R. D. MITCHELL				
26-1	Vacuum Deposition for Window Films / 557 A. TAYLOR				
26-2	Metallized Polyester for Food Packaging / 561 S. H. ROUNSVILLE				
26-3	Metallized OPP Film, Surface Characteristics and Physical Properties / 563 J. V. MARRA				
26-4	Browning and Crisping Packages for Microwave Cooking / 569 T. H. BOHRER				
26-5	Metallizing for Packaging, Recent Technical Advances / 577 A. A. BROOMFIELD				

26-6	Growth in Film & Paper Metallizing / 579 C. A. BROEMEL					
27	Statistical Quality Control - Panel Discussion / 581 J. V. BENHAM					
28-1	Water Base Coatings: Problems and Solutions / 583 N. C. SMITH					
28-2	Some Unique Features and Applications of Novel Ethylene Vinyl Chloride Latex Emulsion / 587 R. DERBY, W. J. HOOK, J. G. IACOVIELLO and B. R. VIJAYENDRAN					
28-3	Polymer Emulsion Blends as Adhesives for Flexible Packaging / 593 J. S. MORPHY, T. M. SANTOSUSSO and D. J. ZIMMER					
28-4	Development of New Waterborne Laminating Adhesive Systems / 601 A. C. MAKATI					
28-5	Structural Investigation of Waterproofing Resins Used in Starch Corrugating Adhesives / 609 T. O. MURDOCK, D. C. JOHNSTON and H. BERVEN					
29-1	Polybutylene Blends on Easy Open Seal Coats for Flexible Packaging and Lidding / 613 C. C. HWO					
29-2	Toughened PET for Barrier Films / 615 D. L. McCAULEY					
29-3	Ultra Low Density Polyethylene for Film Extrusion / 627 L. D. CADY, B. A. SHAH, and J. A. DEPOY					
29-4	Prediction of LLDPE Blown Film Performance / 639 D. V. BIBEE and K. K. DOHRER					
29-5	A Morphological Study of PVDC/PE Blends / 649 D. E. KIRKPATRICK and D. RANCK					
30-1	State of the Art Continuous Adhesive Compounding / 653 J. SCHAK					
30-2	The Evolution of Pressure-Sensitive Adhesive Spray Technology / 661 J. RATERMAN					
30-3	Comparative Study of Microcrystalline and Synthetic Waxes in a Hot Melt Adhesive / 665 J. W. NICHOLS, T. R. GRAVES, H. L. BARNES and J. G. McCORMICK					
30-4	New E. B. Curable Pressure Sensitive Adhesive as an Alternative to Solvent and Emulsion Coatings / 671 F. S. McINTYRE					
	Conversion Factors for SI Units / 673					

TREATMENT REQUIRED FOR PRINTING WITH WATER-BASED INKS

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ABSTRACT

Printing with water-based inks has caused renewed concern regarding the reliability of current methods of determination of wettability and adhesion. Standard ASTM methods of determination of surface tension no longer provide the necessary information when retreating film at the printing press. A new method is being developed to provide both criteria of testing and meaningful information regarding wettability and adhesion.

INTRODUCTION

To understand the impact of water-based inks, adhesives and coatings on the testing and production processes in the converting industry, one must begin with the equilibrium established between poly substrates and solvent-based materials. When poly substrates were first introduced, the converting industry was faced with wettability and adhesion problems between the substrates and coating materials (inks, adhesives and coatings) then in use. The solution to these problems involved an evolution of processes, procedures and material formulations that eventually resulted in an inter-related system of compatible substrates, coating materials and processes that provided reliable production of converting products.

Substrate producers found that in addition to developing products of consistent gauge, opacity or clearness, moisture barrier characteristics, machinability, etc., they were also required to insure that surface characteristics allowed for acceptance of coating materials. Surface treatment processes were developed — flame treatment, spark-gap treaters, metal electrode treaters, and, finally, bare-roll treaters — that permitted substrate producers to supply converters with polys having well-defined characteristics.

Simultaneously, coating material suppliers were called upon to develop a series of inks, adhesives, and coatings that were compatible with the substrate characteristics the state-of-the-art could then produce. Through experimentation and hard work, a series of various solvent-based materials were formulated that had sufficient wettability and adhesion along with the gloss, opacity or clearness, machinability, etc., required.

The controlling parameter between substrate surface and coating material acceptability became dyne level measurement. The most widely used test for substrate surface characteristics was defined by the Wetting Tension Test as outlined by ASTM D2578. Through the use of various formulations of formamide and cellosolve mixtures, the substrates wetting tension in dynes per cm could be determined. Coating material manufacturers also provided products of well defined dyne level. As a result, and after some period of experimentation and production experience, a common rule-of-thumb became accepted that stated:

For proper wettability and adhesion, the substrate wetting tension should be approximately 10 dynes higher than that of the coating material.

Although the constant pressure for product improvement and cost reduction introduced some stress in the system, for the most part the converting industry had achieved a measure of equilibrium between substrates, coating materials and test and production processes.

Water-Based Materials Impact

That equilibrium is now upset by environmental considerations that are gradually legislating the reduction or elimination of solvent-based coating materials. As a result, coating materials manufacturers have developed and are continuing to expand and improve a series of partially water-based and 100% solid materials.

So as not to mislead the reader, the author would like to mention that solvent recuperative systems which permit recovery for purification and reuse or disposal or incineration are available. Current technology in that equipment requires extensive machine retrofitting and relatively high cost additional equipment. As a result, only very high volume converters or those with specialty end-products are finding recuperative systems economically viable for answering environmental restrictions. The vast majority of converters and, I might add, commercial printers, will find water-based materials technology the most acceptable resolution to environmental emissions restrictions.

WATER-BASED MATERIALS: PROBLEM DEFINITION

As described in the introduction, solvent-based materials were an important element in an interrelated system of testing and production procedures that facilitated reliable converting processes. The change to water-based materials has impacted the other elements in the system and new procedures and processes are already being developed and tested to provide a new equilibrium of characteristics between poly substrates and coating materials.

Substrate Surface Characteristics Analysis

In attempting to re-establish the equilibrium between substrates, coating materials and testing methods to establish consistent, measurable parameters for both, many of the theories, assumptions and generally accepted rules of operation have been reexamined and questioned. Experimentation and laboratory testing done in the past has been reviewed and much new work has been done. However, these basic questions remain:

- By what mechanism does corona treatment produce improved bonding between substrate and coating material?
- 2) What is the specific relationship between wettability and adhesion?
- 3) Do Wetting Tension Solutions provide accurate and sufficient measurement of surface characteristics that affect printability and adhesion?

If we review, summarize and correlate the work that has been done, we can establish a practical system of operation that assures reliable, repeatable results for most converting operations on most substrates. And, by implication, if not by specific data and proven theory, we can begin to answer the above questions. Certainly, we can provide a framework for future study that will result in more definitive answers to those questions.

The new water-based and 100% solid coating materials exhibit an increase in surface tension characteristics over the previously used solvent-based materials. Most water-based inks are now formulated for wetting tensions between 32 and 40 dynes since all contain some solvent, usually alcohol, in addition to water. This fact focuses attention upon the surface tension characteristic of the various substrates used in converting processes. How can substrate surface tension be increased at the time of converting? What factors affect substrate surface characteristics?

Tested Factors Affecting Substrate Surface Characteristics

There is general agreement that corona treatment will improve the wettability and adhesion characteristics of most poly films. The reason for this improvement is subject to some debate but, even here, there appears to be underlying agreement.

Morphology. Surface roughness was, at one time, thought to be increased by corona treatment. This is now found untrue through extensive Scanning Electron Microscope viewing of surfaces before and after corona treatment. 1.2.3

Surface molecular analysis. Electron Spectroscopy for Chemical Analysis (ESCA) has shown a linear relationship between surface oxidation, i.e. oxygen available at the surface, and wettability and adhesion. 1.2.3.4 This analysis has been correlated with theories of surface energy level and the availability of polar sites at the surface. 3.5 However, unpublished experiments with corona treatment in nitrogen atmospheres and in vacuums demonstrates increased wettability and adhesion ostensibly without increasing oxygen at the substrates surface. Whether nitrogen can perform a similar function as oxygen in increasing surface energy is yet to be shown. Also, the energy increasing mechanism of vacuum treatment is not yet defined.

Additives. Experimentation has demonstrated that the impact of additives on poly film surface characteristics varies with both the type of additive and substrate. Significantly, certain combinations exhibit a negative impact on wettability but do not seem to affect adhesion of either solvent-based or water-based inks. This situation is supported by actual experience in the production environment.

Unpublished experiments dealing specifically with slip additives seem to indicate the following:

- Additive Concentration vs. Bloom Time (time in which additive migrates to the surface) is variable until a threshold of 1000 PPM of additive is reached.
- 2) In any case, blooming appears to occur within 24 hours.
- Corona treatment appears to encourage blooming of the slip additive to the treated side of the substrate.
- Slip additives do negatively impact both wettability and adhesion.
- 5) Secondary treatment (to be discussed later) counters the negative impact of slip additives on wettability and adhesion which, in most instances, allows the use of water-based coating materials.

These experiments have not been completed and the above results are tentative.

Effect of contact and time. Experience has shown that all corona treated films lose treatment, as measured in dynes, over time. Experiments have demonstrated that treatment is lost in two stages — first, by contact of the treated surface with a machine roll and by contact with the untreated surface when wound and secondly, through aging over time. In one experiment, ESCA measurements demonstrated a 5 to 24% decrease in oxygen levels over a seven week period with a corresponding reduction in wettability. However, adhesion properties were not changed by the decrease in oxygen levels.

Surface treatment test method. Testing of surface tension utilizing wetting tension solutions per ASTM D2578 has long been recognized as the most practical method for most converters in the production environment. Recently this test method has been questioned from several standpoints.

First, the materials used, formamide and cellosolve, have been found to be toxic. Although not highly toxic, care should be used by all who are asked to work with these solutions. Special care must be taken by pregnant workers or women in their childbearing years. In fact, it is a reasonable precaution to remove these workers from all contact with the solutions.

Secondly, there are serious questions on the accuracy and, therefore, the value of wetting solution testing.^{5,7} These concerns are centered on two recently observered developments/factors:

1) Practical, in production experience, has demonstrated that wetting solution dyne readings do not, in some cases, accurately indicate printability and adhesion with water-based materials. In some instances, secondary treatment (Figure 1) has shown little or no substrate surface tension improvement when measured by wetting solutions. Yet, in every case, printability and adhesion of the substrate have improved dramatically.

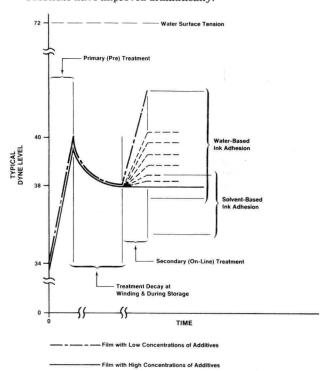


Figure 1: Effect of Secondary Corona Treatment

2) Tendency for substrates to contain greater amounts and more additives than previously used. These additives are thought to mask true surface characteristics and to contaminate wetting solutions such that inaccurate readings result.

The reasons for inaccurate or inconclusive readings with wetting solutions have not been fully documented. The solutions are finely balanced mixtures of the two components which have very specific wetting tensions. Contamination by even small amounts of moisture or additives would alter readings. In the production environment, contamination could easily occur. Also, ambient temperature and temperature of the solutions and substrate at the time of readings must be closely controlled for true readings. However, there seems to be growing opinion that wetting solutions do not accurately measure all the surface characteristics that determine wettability and adhesion.

An old/new method of surface treatment testing. To establish a new equilibrium between substrate surface characteristics, coating material characteristics and production processes and methods, an accurate method of testing is required. Some years ago Dr. William A. Zisman working with equations developed by Thomas Young developed the mathematical and practical underpinnings of testing surface tension using accurate contact angle measurement. Zisman's work cannot be fully exposed or discussed here, but Figures 2 and 3 provide a simple demonstration of the theory. Much of the experimental work done over the past few years has ignored wetting tension solutions as a method of surface tension measurement in favor of contact angle measurement. La, 3, 5, 6 Currently, several companies are marketing devices for accurate contact measurement.

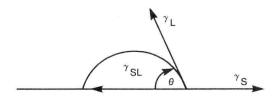


Figure 2: Substrate Surface Tension Greater Than Liquid Surface Tension

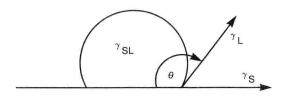


Figure 3: Substrate Surface Tension Less Than Liquid Surface Tension

$$\gamma_L \cos \theta + \gamma_{SL} = \gamma_S - \pi_e$$

Where: $^{\gamma}$ L, $^{\gamma}$ S, and $^{\gamma}$ SL are the free energies of the liquid and solid against their saturated vapor and of the interface between liquid and solid respectively $^{\pi}$ e is the equilibrium pressure of the absorbed vapor of the liquid on the solid θ is the equilibrium contact angle.

TREATMENT PROCEDURE DEMONSTRATING PRACTICAL RESULTS

Although much work needs to be done in scientifically validating current relationships between substrates, coating materials, and methods, the converting industry cannot stand still to await the results. Further, all three elements are themselves changing to meet practical production requirements.

What has evolved is a method whereby substrate producer, coating material manufacturer, and converter, working in conjunction with treating equipment suppliers, have each assumed a portion of the responsibility for making the system work. The system works like this:

- The substrate producer provides surface treated substrates generally with higher surface tensions than previously supplied. Because of problems with blocking, back-side treatment, additive content and blooming, etc., the substrate producer cannot provide polys with sufficient surface tension to allow successful implementation of all converting processes.^{4,5}
- Coating material manufacturers, especially in the area of water-based inks, have developed formulations that provide reasonably low surface tension despite the high surface tension of water (72 dynes).
- 3) Converters and commercial printers are now retreating (providing secondary corona treatment) to increase printability and adhesion in line.⁴ Although, as stated previously, the effect of secondary treatment on wettability as measured by wetting tension solutions varies (Figure 1), as a practical fact, converting operations at typical line speeds can be completed successfully with secondary treatment. Without secondary treatment most converting processes cannot be successfully completed at typical line speeds.

In addition, those converters and commercial printers who use a variety of coating materials will find that solvent-based, as well as water-based, coverage and adhesion improves as a result of secondary (in-line) corona treatment. In some cases this will allow higher line speeds with no degradation of product quality.

CONCLUSION

The whole story is yet to be written and, with the usual pressures for cost reduction and product improvement, will probably never be written. However, it can be stated unequivocally that the procedure described works with the current state-of-the-art and will improve because of the continuing efforts of all concerned. Converters can face the future with its increasing environmental restrictions secure in the knowledge that their needs are being and will continue to be met by materials and equipment suppliers.

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Panel Discussion

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UV CURING SYSTEMS: BASICS to RECENT ADVANCES

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ABSTRACT

Several aspects of UV curing systems, and their relationship with label making and product finishing are presented with some basics of UV sources, including the microwave powered lamp. The selection of different spectra can be used to produce markedly different results in cured products, such as improved surface properties, depth of cure, and adhesion. The benefits of the use of UV for label-making, incorporation of curing systems into equipment, as well as safety aspects are discussed. Some of the latest activities in the continuing development of UV materials technology are: waterbased UV curable materials, UV curable silicone release coatings, and gloss control using different wavelengths of UV light.

INTRODUCTION

UV curing, or photopolymerization, is the process in which inks, coatings, and adhesives are cured by means of short wavelengths of light.

High intensity ultraviolet (UV) lamps first became commercially available in 1970 and the number and types of applications have expanded and grown ever since. Commercial UV ink and coating applications are now in common use for plastic and glass containers, circuit boards, optical fibers, labels and release papers, as well as use by a growing number of sheetfed and web printers.

UV assembly adhesives, electronic component marking, dental and medical uses, topcoats for flooring, photopolymer printing plates, bonding, coating and decorating of automotive components, coatings for optical data storage media, and beverage can decoration are a few of the diverse uses of UV curable materials today.

UV is found in labelmaking in a number of steps of the process ranging from pre-press proofing, photopolymer plate-

making, laminating adhesives, release coatings, and finally, inks and varnishes.

CONVENTIONAL vs. UV

Conventional thermally cured inks or coatings are composed of a resinous binder, pigments and fillers, and diluent solvents. After application to the substrate, heat is applied, driving off the solvents and curing the coating film. The evaporated solvents are generally flammable and toxic, and must be considered pollutants. These solvent emissions require the use of even more energy to be burned or "scrubbed" and recovered by distillation.

A UV curable system achieves the transition from liquid to solid by means of a chain addition polymerization, triggered by a photochemical interaction, in which the photoinitiator is the active component of the material formulation. It is the energy absorber which starts the reaction when exposed to ultraviolet light. In UV curable material, the resin binder is replaced by a formulation of liquid monomers and oligomers, into which the pigment can be dispersed. The coating is completely reactive and the amount, or thickness, that is laid down wet is, essentially, the same as the thickness after curing.

LAMP SYSTEMS

In addition to the UV chemistry of the ink, coating or adhesive used, a most important part of the UV system is the lamp system itself. A well-known and widely used type of lamp is the mercury vapor arc lamp. In this type of lamp, clear fused quartz tubing is used to enclose the plasma that produces the ultraviolet energy. The fused quartz tubing has a wall thickness of about one millimeter and an outer diameter of 20 to 25 millimeters. The ends of the quartz tubing are sealed around the electrode ribbons to provide a vacuum tight enclosure.

When power is applied to the lamp, the voltage across it rises until ionization of the starting gas occurs. As the lamp warms, the plasma changes from that of the starting gas to a constricted mercury arc.

Another type of lamp, equally well known, is the electrodeless lamp. This type of lamp is distinguished by the fact that it does not rely on a

sustained high voltage arc between electrodes; it is powered by microwave energy.

The electrodeless type of UV lamp requires no direct electrical connection for excitation. It is a simple, sealed quartz tube, containing mercury and gases and other metals, as desired. The tube, or bulb is mounted within a cavity formed by an elliptical reflector. High power microwave power tubes are coupled to the reflector cavity; when the microwave energy is "turned on" the lamp absorbs sufficient power to generate a plasma within the quartz envelope. It can be turned on and off nearly instantly, eliminating the need for shutters required by arc lamps.

The bulb is made of quartz and has a tapered shape which optimizes its UV, thermal, and microwave absorption properties. The bulb has an inside diameter of only 9 mm. The short quartz tips at either end of the 25.4 cm (10 inch) bulb provide mechanical support for quick mounting into spring-loaded receptacles. However, they are not electrodes and have no electrical function.

The top of the reflector contains two rectangular slotted holes through which microwave energy is transmitted into the cavity. The source of microwave energy is two 1500 watt magnetrons (oscillator tubes) located in the top half of the irradiator assembly. These magnetrons operate at the same frequency as microwave ovens and perform a similar function. Cooling air is fed through each magnetron and into the lamp cavity through an array of cooling holes.

The air flow provides cooling for both the magnetrons and the bulb envelope. In addition, the filtered air flow provides a positive pressure in the reflector and bulb area, helping to keep the surfaces clean and reducing required lamp maintenance.

Because the microwave powered bulb has no electrodes, there are no materials to react with the highly energized plasma inside the bulb. This means no contamination which would deteriorate the bulb output or shorten its lifetime, and no deterioration or darkening of the bulb ends which would be caused by condensation of vaporized electrode material. Electrodeless bulbs are known for their stable output and long life.

DIFFERENT SPECTRA

A major advantage of the electrodeless lamp is that it can accommodate a wide variety of fill materials, which allows a broad choice of spectral output. Lamps with special fills are readily interchangeable and offer the possibility of tailoring the curing spectrum to the specific coating application.

Several spectral ranges of lamp output are available with the electrodeless lamp (Figure 1): the "H" bulb has a strong output in the short UV wavelenghts, and is similar to the spectrum of a mercury vapor arc lamp. The "D" bulb output is rich in the 350-400 nanometer wavelength range, while the "V" bulb is strongest in the blue visible range of 400-450 nanometers.

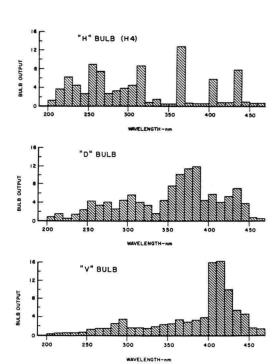


Figure 1. Spectral Output of Several Bulbs

It has been found that significant differences in curing results are achieved with different bulb spectra. Clear coatings and varnishes develop the best surface properties, such as scratch and abrasion resistance, when cured with the "H" bulb. Pigmented materials, inks and paints are cured more deeply, and can achieve better interlayer adhesion

with "D" bulb exposure. A white basecoat, for example, usually containing titania, may cure 3 times faster or 3 times deeper with exposure to a "V" bulb than when cured with the "H" bulb.

The reason for this occasionally unexpected behavior of lamp and material combinations lies in the fact that the UV sensitive materials, particularly the photoinitiators, are also UV absorbers. The UV energy which cures the outer surface may, in fact, be prevented from penetrating further into the material. Longer wavelengths exhibit the ability to penetrate more deeply and yet have sufficient energy to initiate the polymerization reaction. This characteristic is of distinct benefit for screen printed labels, where the rich, opaque ink decoration has a quality appearance and appeal to the consumer.

CONTROLLED GLOSS

Requirements for carefully controlled flatting of the surface finish for wall-board, furniture components, and plastic film has stimulated development of materials which give the desired matte finish. These materials usually require an inert (oxygen free) environment for curing.

Using the wavelength principles described above, the degree of flatting of the surface can be controlled entirely by the curing system exposure(1) and concentration of flatting agents in coatings which do not require nitrogen inerting during cure.

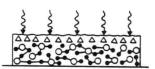
Flatting agents, usually silicates, are incorporated in the coating (Figure 2). Initial UV exposure consists of wavelengths specifically within the near-UV region of the spectrum which cure effectively in the lower layers of the coating while driving flatting materials to the surface. After a controlled time, subsequent exposure to shorter wavelengths will "stop" the process and complete the surface cure. Control of the time (distance) between the two cure steps controls the deglossing of the coating. Control of 20 gloss units (2) over a range of 10 to 90 gloss units can be easily achieved.



Liquid film of UV curable coating before exposure to UV light.



Type I irradiation: deep penetration cures lower layers. Flatting agents migrate to surface.



Type II irradiation: surface now cured with flatting agents at surface.

Figure 2: Controlling Gloss with Two UV Exposures

LIGHTSHIELDING and ADAPTATION to PRESSES

Incorporating UV lamps on web offset presses or web letterpress equipment calls for an enclosure which will hold the lamp (or lamps) and provide a shield for the UV. This enclosure, called a light shield, may be located after each print station, if UV inks are used, to cure each color prior to application of the next.

If UV varnish is applied, a final cure is located after the coating station. UV varnish is quite commonly used over conventional inks, combining the desirable finish properties of the UV varnish while utilizing the lower cost conventional inks.

Lamps usually extend over the full width of the sheet or web. With modular UV lamps, modules are placed end-to-end to create the desired cure width capability, and without curing gaps between lamp modules.

SAFE USE

Design of UV curing equipment for safe use is comparatively easy. The enclosure is constructed so that the least amount of light is emitted from it.

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⁽¹⁾ U.S. Patent No. 4313969 and Foreign Patents Pending.

⁽²⁾ Measured by 60 Degree Gardner Gloss