History of Roll-to-Roll Vacuum Coating

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INTRODUCTION

The vacuum roll coating industry, as we tend to think it today, has come a long way since its conception, which appears to have been in the early 1930's. The progress driving its advancements came from many different areas. These include advances made in equipment design, material developments, process monitoring and control designs and market demands. Some of the other dynamics driving this market were lower cost, substantial in some cases, flexibility of the final product, performance properties of bulk materials at tremendous weight savings and the ability to create materials with unique properties that could not be reproduced in the bulk state. This presentation will attempt to cover some of these advancements and mention some of the companies that contributed so much to the growth of this industry. Much of the information gathered for this study is anecdotal in nature and thus has no formal reference. An expanded version of this presentation can be found in the SVC's book covering the last 50 years of vacuum history and that of the SVC itself. The papers and comments gathered during the research done for this paper will be given to SVC for their achieves and should be available to anybody who is interested in them.

As best as I can tell the total roll to roll vacuum coating market was in excess of $4 Billion dollars in 2005, my latest numbers. This number is for the finished product and not just for the vacuum coating component itself. This is because almost all of the final end uses of these vacuum coated films have other value added steps applied to them to enhance the products performance.

EARLY HISTORY

Commercial vacuum roll coating appears to have gotten started in the early 1930's. Most sources indicate that a Hungarian scientist, Paul Alexander, was the inventor of the first roll to roll vacuum coater. He later moved to Belgium and then to the United States, where he continued his research at Princeton University. He also started a company called Alexander Vacuum Coatings. This company was later bought out by Continental Can, a pioneer in the use of vacuum metallized coated paper for label stock.

While still in Europe Mr. Alexander had two roll coaters made by Konrad Kurz, a German company. One of these was shipped to Bavaria and the other to Cecil Whiley in England. The original purpose of this machine was to develop a replacement for gold leaf that was then made by manually hammering out gold sheet to very thin layers. The vacuum coater could product as much gold leaf in a day as the manual process could in a week. The substrate was glassine, with the coating rate being 400 sq. M in a 24 hour period. A popular use of this material was for monograms for men's hat bands.

Another product developed using roll to roll vacuum coaters was decorative gift wrap based on silver. Silver wire was wrapped around a metal rod. The rod was resistively heated until the silver would start to evaporate from the wire. The process was then referred to as sputtering.

World War II provided yet another market push for the use of vacuum metallizing using roll coaters. Radar guided AA guns were being introduced and were proving to be quite accurate. It was found that the radar tracking could be thrown off if large amounts of aluminum chaff were ejected from the airplanes. Bundles of Al foil with an explosive set in the middle were rejected from the plane, the explosive was set off and the foil was supposed to disperse over a large area. There were two problems with this approach. The first is the foil tended to stay agglomerated and did not disperse well. The second was the overall weight of the bales. It was found that aluminum coated glassine, a much lighter material, would disperse much better and had the same radar reflection properties of the foil. It was also discovered by Bosch that capacitors, of which there are many located in an airplane, could be made from aluminized glassine. This discovery also resulted in significant weight savings for airplanes.

During World War II, the United States government voided all German based patents held in the United States. As a result of this all of the work done in Germany on roll to roll vacuum coating became public property. Taking advantage of this companies such as Hy-Syl (later to become Madico and then Lintec), National Research and Continental Cans got their start. Many of these companies used paper as the substrate to be coated for use in label stock.

Its rough surface resulted mainly in a dispersed reflection, not the bright shiny reflection the end user wanted. This problem was solved by coating the paper surface with a smoothing

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layer, normally a lacquer. This was the source of the infamous knick name that a close colleague of many of use in the Society, Michael Hansen gave to the SVC. He called it the "suck and spray" society.

THE EMERGING YEARS

During the 1950's and early 1960's many technical advances were made in the vacuum roll coating industry. The original roll handling designs were very primitive. Coating speeds were limited to levels of 3-4 lineal meters per minute. The vacuum pumping systems were based on diffusion pumps that used either glycerin or mercury as the working fluid. Pump down times took hours and the pumps had a hard time handling the out gassing of the natural based substrates. The thermal evaporation boats were just carbon. Molten Al is a very corrosive material and would easily dissolve the carbon. Their expected life time was about 1 hr. Al wires feed systems were also very crude and the purity of the original Al wires was suspect at best. The best production cycles lasted at most several hours. All of this was soon to change.

First the equipment manufacturers figured out how to isolate the unwind and rewind chambers from the coating chamber. Secondly they started to make significant improvements in the film handling systems, getting the coating speeds up to the 100 M per minute range. In contrast to this, today's thermal metallizers are running at rates close to 1000 lineal M per minute, with pump down speeds of 12-15 minutes and turn. Some of the companies instrumental in developing these new machine concepts include, but are not limited to, Leybold Hereaus, (created when Leybold and Hereaus merged in 1967), National, General Engineering, Ulvac, Galileo, Dusenbury, Airco and Van Ardenne. There were also a lot of improvements made by end users who chose not to disclose much information publicly do to fear of teaching their competitors. Some of these companies include Gomar, Scharr Industries, National Metallizing, Camvac, Continental Can and American Can. As an aside, it should be pointed out that several designs for air to air roll flexible substrate film coaters were built during this time. Airco and Ulvac built the ones the author knows about. The problems were the tremendous pumping requirements needed and the damage done to the substrates as they went through the air locks.

Halogen based hydrocarbon oils were developed for use in the diffusion pumps and Root blowers were added to the pumping scheme. In the mid 1950s Metallwerke discovered that if you coated the carbon crucibles with a top coat, based on either tungsten, tungsten carbide or boron nitride the life time of the boats could be significantly improved. Union Carbide took this one step further by fabricating the boats out of boron nitride or titanium diboride. Today's boats last up to one shift despite the tremendous increase of power that is now being used with them.

Finally there were the developments made in the flexible substrates being coated. The introduction of PET films probably had the biggest impact. It was vacuum compatible, relatively flat and smooth and had very little out gassing. The use of this film really helped accelerate the growth of vacuum coated Al in the packaging industry, now the largest volume market for vacuum metallized films that exists today. Following the introduction of PET came that of OPP. This substrate was slightly cheaper because PP has a lower density then PET, so you get more sq. M per kilo yields. It doesn't have as good physical characteristics as PET does, but is quite adequate for many packaging applications. OPP helped fuel the growth of packaging based films even further.

THE NEXT STEPS

From the 1960's to the 1990's: By the late 1960's many companies began to realized that there were certain limitations in the use of thermally evaporated AL films. They were fine for opaque packaging and semi transparent packaging for such uses as microwavable films. However, in emerging applications such as solar control films, or other products that required highly transparent conductive coatings, like updatable microfiche, ionographic X-ray imaging, electrostatic printing and touch panels they were not satisfactory. The AL based films were too reflective and not very environmentally stable in the higher resistivity ranges that many of these applications required. Also the use resistively heated boats have very limited uses for other materials than Al. Limited success was had with Ag and Cu, but the same process speed and productivity could not be achieved with these other materials.

It was soon discovered that planar magnetron sputtering, and later rotatable magnetron sputtering, could be used to deposit a much wider variety of materials, although at a much lower process speed. Airco (1974) and John Chapin (1979) are given credit for inventing the planar magnetron, with Chapin having the earlier priority date. Shatterproof was granted the patent rights for the rotatable in 1982.

The advantages of a greater list of material candidates to select from, with lower reflectivity, a variety of performance capabilities and more stable environmental properties outweighed the cost disadvantage in many applications. But Al remained the dominant player in the packaging industry, which was very cost sensitive and wanted the high reflectivity for decorative purposes. Also the opacity of the AL coating helped protect many of the packaged materials from damage due to sunlight exposure.

In 1974 the Polycold refrigeration panel was introduced to the market. This is device is considered as one of the major breakthroughs in the roll to roll vacuum coating process. The refrigerated panel acts as a very efficient trap for volatile gases in the vacuum, especially water vapor. It is in wide use today.

Around the same time several companies began to work on depositing indium tin oxide (ITO), in a semi conductive state, to fabricate a highly transparent oxide layer. This was the answer to the requirements of a high transmission, low reflective stable conductive coating required by the product concepts mentions above. The first ITO coating were deposited from ceramic based ITO targets. The problem with this approach was that the quality of the ceramic ITO was rather poor and the targets would crack and debond regularly. The author was involved in many experiments were the run would have to be stopped prematurely when a loud "gong" was heard as a piece of the target fell off the cathode and hit the chamber wall. Because of this and the relatively high cost of ceramic targets a process of reactive sputtering using an InSn alloy target and a reactive sputtering gas was developed. This technique offered significant cost advantages over the ceramic based technology and produced the same quality film. It wasn't until the 1990,s that the flat panel LCD market grew large enough to push the ceramic target manufacturers to develop high quality ceramic based ITO target for their products. So now, either the ceramic or reactive process can both be used.

In the meantime, the solar control industry started to develop a variety of sputtered materials to produce a wide selection of lower reflective, stable films. By 1978 Southwall had successfully developed a 3 layer dielectric/metal/dielectric stack, first invented by J. C. C. Fan of MIT for use as a heat mirror film. Such a film will pass a significant amount of visible light, but reflect infrared light. This makes it the ideal material to allow visible light to pass through, but to minimize the amount of infrared radiation, or heat transmitted through the stack Southwall later refined the technology to a 5 and then a 7 layer dielectric stack. Each addition set of layers improved the amount of visible light transmitted and the amount of heat rejected. According to the author's sources, Southwall placed the first order of an 80" wide commercial production vacuum roll coater with Leybold Hereaus in 1978. The coater was commissioned in 1980.

In the mean time Sierracin Intrex had developed the roll to roll coating process of depositing ITO to the point were they placed the second production commercial vacuum roll coater order with Leybold in 1982. It was for a machine based on reactive sputtering with three cathodes, and a net 48" wide web and was commissioned in 1985. Sierracin got its start in vacuum roll coating in 1964 by developing a multi point e-beamed thin layer of Au film deposited on PET film. It intended use, once over coated with a sol get based AR coated layer, was to be used as an inter layer transparent heating element for use in front window of cars. By the late 1960's 50,000 Lincoln Continentals and Ford Thunderbirds were on the road with these windshield. Than the original oil crisis hit and Ford made the decision that they would drop any option that could not be used across their model selection. Thus the business disappeared over night. This is time Bill Kittler and the author got involved in vacuum roll coating while at Sierracin.

Martin Processing, initially using thermal evaporation of Al, decided to explore sputter roll coating in the late 1970's. Martin Taylor helped them converted a Dusenbury built thermal evaporator with a sputter cathode in 1979 and had enough initial success to justify placing order for an 80" sputter roll coater from Leybold in 1985

By 1985 Coulter reported the production of a CdS based photovoltaic solar cell deposited on a stainless steel film using RF sputtering in a 12 cathode coater produced by Leybold. Ben Meckel of DTI, an independent and very private inventor, had built two 80" free span coaters built in house for making solar control films and satellite thermal control materials. This operation was later sold to what is now Bekaert Specialty Films. BSF and CP Films (evolved from Martin Processing to Courtaulds Performance Films to CP Films) are now considered to be the 2 largest solar control film businesses in the world. The Meckel coaters ended up at Techni-Met.

During this same period of time Sheldahl developed a series of vacuum coated films that were used in mainly in aerospace applications. These materials had the optical properties of bulk materials, but were much lighter and flexible, both attributes that the aerospace and satellite markets found very attractive. One of their more interesting coatings was a flexible barrier for mono atomic oxygen. This is a very aggressive chemical that would rapidly attack any plastic found on the outer surface of a low earth orbit satellite. They were quite successful in this effort.

By the early 1980's Optical Coatings Laboratory (OCLI) became very interested in vacuum roll to roll coating. They developed a material known as Optically Variable Pigments. It took a very intense 4-5 year development program before the first commercial pigments were sold. The process involved depositing the pigments on a PET film carrier and then removing the pigments in flakes from the carrier. The flake was then mixed into and ink based carrier. This material is now the world leader in anti counterfeiting technology, especially for currency, bonds and other sensitive documents. OCLI also produced a wide variety of other thin film products used in applications such as window films and photocopies.

Other vacuum roll to roll manufacturers that got their start during this time frame include 3M and IBM who were both very active in this field, with 3M still playing a significant roll. Techni-Met and VDI are two other companies that are still very active in this area. Tech-net met was spun out of Scharr Industries in the mid 1990's and has had great success in sputter depositing a wide variety of metals for numerous applications. VDI is a privately held company that has been in existing for a number of years, also provides many different coatings to various industries.

During the early 1980's sputter roll coating began to develop in Japan. This effort was lead by Toray and Teijin. Teijin later licensed their technology to Oike. Nitto Denko and Toyobo also started up their own sputtering operations. Gunze and Sumitomo Bakelite both developed ITO capabilities, but their production is used mainly for in house applications. These Japanese companies concentrated mainly in the manufacturing of ITO. Teijin Chemical has recently re-entered the business as well. Some roll to roll sputter coating capabilities are also now developing in Korea.

Also in the 1980's GE developed a novel coating technique called PML, standing for polymer based multi layers, that used alternating layers of a vacuum deposited and cured polymer layer and an inorganic layer. The technology was original developed to make capacitors. GE exited this business soon after and licensed this technology to others. It eventually ended up with Catalina Coatings, Sigma Technologies and Battelle Northwest. The most popular end use of this technology is to make high barrier vapor layers.

In 1992 Airco developed a system to deposit SiO_2 layers using plasma enhanced chemical vapor deposition (PECVD). The resulting film proved to be a very good vapor barrier that could be made at reasonable speeds. One of its advantages is that it was non metallic and could be used in microwave applications. The initial work was carried out by John Felts, et. al. Several commercial coaters were produced and shipped to Japan. Later General Vacuum licensed this technology. The PECVD technique is proving to be the process of choice now for producing ultra high barriers required by the OLED market. GE and Dow Corning have announced some exciting developments in this area over the last few years.

In the mid 1980's a very novel application appeared. The US government was looking for a film that could be used to help promote stealth properties in their airplanes, helicopters and even ships. Such a film could be made, albeit with some difficulty, by sputter roll coating. Southwall and Andus are two vendors that the author is aware of that participated in this program. However it was a top secret effort, so not much cross fertilization occurred. However, once the Berlin Wall came down and the cold war started to go away, these programs disappeared rapidly.

One more important technical break through that came during this period should be mentioned; this is the use of electron beam coating sources. As far as the author can tell this process got its major start at Von Ardenne where it was used to coils of strip steel. During the 1970's in to the early 1980s considerable work was done with electron beam deposition sources to make "vertical domain" magnetic storage tape. Most of this effort, while it originated in the USA, ended up in Japan. In the 1980's the improvements made in these sources and their increased reliability allowed them to be used in high volume Al deposition. There are now some electron beam coaters that are at least 2-3 meters wide. Used in conjunction with a reactive plasma the evaporated Al material can be converted to Al oxide for transparent barrier applications. It should be noted that Roger Kelly, then of Camvac, was the first to develop the reactive metallization to make transparent barriers.

One cannot close this section without mentioning the establishment of the WEB TAC at SVC. Five colleagues got together in the mid 1980's to discuss the need to create a forum were vacuum roll coating could flourish. These were John Fenn, Alan Taylor, John Marcantonio, Bob Cormia and John Matteuchi. This TAC has grown significantly since its inception in 1987, and promises to continue to make contributions to the vacuum roll to roll coating industry in the future.

CONCLUSION

The vacuum roll to roll coating business has proven to have a very complex and exciting history. While the author has tried to touch on many of the events, products and companies that helped to weave this story, it is without doubt that many contributions have been left out. He is sorry for this. There were as many dead ends in this growth as there were successes. One the dead ends the author was involved in was the development of a transparent electrographic film to be used in wide bed electrostatic printers. The end product was to be used to directly generate engineering drawings, particularly for the aircraft industry. The problem was that the Rs of the conductive coating had to be in the megohm range and be environmentally stable. This was a very interesting problem, but the engineers at Andus Corp. solved it within 6 months. However, just as the film was about to be introduced to the market a new technology that used a slurry of ITO particles in a solvent carrier was introduced. The vacuum based product could not compete in price and the demand for it disappeared over night.

It should be pointed out that the industry has been advancing the technology of vacuum roll very rapidly over the last few decades. We were dealing in nano technologies before the word became popular. However there are new challenges ahead that we must be aware of. Nano particles, conductive polymers, and printed electronics are in the forefront of the progress being made in designing and developing new products and processes. Sumitomo has just announced a ambient solvent applied transparent film that appears to have equal to or better Rs vs VTLration than ITO and is very extendable. It is not in full production yet, but they are making promises of having high volume samples of the "ink' by the end of 2007.

Vacuum roll coating and these new approaches are most likely going to follow parallel paths in the future. But we have to make sure we continue our progress.

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This presentation is dedicated to the memory of Dr. Bernard Henry, a true friend and renaissance person. He will be sorely missed.