A Novel Lithographic Surface for Use with Thermal Ablative CtP

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Keywords: Lithography, Thermal, Ablation, Polymer, Ceramic

Abstract:

A microscopic investigation of a novel lithographic surface, based upon a polymer-ceramic composite, yields insights into the behavior of a new CtP product from Presstek --- the Anthem® plate. High magnification scanning electron microscope photographs reveal the intricate micro-features that result in a thermal ablative lithographic plate, with a wide press latitude, that requires no gumming step after a simple water wash to remove the ablative debris. Although coated upon a standard anodized aluminum base, this plate uses the surface chemistry of the unique polymer-ceramic composite layer as the actual hydrophilic surface. This layer is composed of a cross-linked hydrophilic polymer embedded with hydrophilic ceramic nodules, which are formed ***in situ*** during manufacturing. This "poly-ceramic" layer allows for rapid roll-up with standard fountain solutions, and run lengths in excess of 100,000 impressions. The correlation between plate morphology and performance is described.

INTRODUCTION:

The rapid changes in requirements for lithographic plates, based upon the needs of the transition to the digital workflow of the CtP environment, have caused manufacturers to seek out new materials and new constructions. The trends toward faster plate production, shorter runs, and more environmentally conscious systems, along with the traditional needs of lower costs and higher reliability, have also fueled this search.

As simpler systems are investigated for CtP, fewer steps and fewer chemicals become requirements. This has lead the way to the search for "no chemical process" plates and thermal / IR imaging with laser diodes.

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Allowing this trend to reach its logical conclusion will also facilitate the trend towards "on-press" imaging.

One such approach toward this goal is the ANTHEM plate which is representative of this new generation of thermal CtP products that use novel materials. [U.S. Patent numbers: 5,493,971; 6,182,569; 6,182,570; 6,186,067; other patents pending.]

DESCRIPTION:

Upon examining the ANTHEM plate macroscopically, it is observed that there is a black coating on lithographic aluminum. **[Slide 1]**

This color is due the incorporation of high levels of carbon black in the plate coating. Carbon is an excellent broad band absorber of light and therefore is capable of imaging with infrared laser diodes with an output in wavelengths anywhere from 800 to 1200 nanometers.

When imaged in a platesetter capable of providing high intensity infrared energy [400-500mJ/cm²] such as the Dimension 400, the laser light is absorbed by the carbon and converted into heat. The high energy density allows a rapid heating of the non-conductive carbon / polymer layer and results in that layer being ablated from the surface of the plate. This reveals the underlying hydrophilic layer. Where not ablated the water insoluble, oleophilic, carbon loaded polymer is retained. **[Slide 2]** This "write white" process results in a "positive working" lithographic plate. The resulting plate has a high contrast black on gray image which is easily read. **[Slide 3]**

LASER ABLATION IMAGING EVENT:

A microscopic view [4,000X] of the plate being imaged in a single pixel mode shows, that even after only 20 nanoseconds into a 110 ns diode pulse, the beginnings of the laser ablation process can be seen as a glowing spot. **[Slide 4]**

After 80 nanoseconds, the eruption of the coating is visible. Well after the pulse has stopped [220 ns], a shock wave continues to expand and the heated ejecta from the ablation are observable. At 510 ns, gas, fine particulates, and larger ejecta are seen expanding upwards. Some of this large material is also seen coming back to the surface of the plate. Once 850 ns have passed, the last remnants of the event are discerned; and by the time 1 μsec has elapsed, the event is over and only the single spot crater is seen.

The materials that were ablated from the surface in this micro-explosion were subjected to intense heating and oxidation. The gases and fine carbon particles are trapped by the appropriate filters. The larger particles that erupted are deposited on the surface of the plate.
Examining the surface of the plate before and after the ablation event reveals some interesting details. **[Slide 5]** Looking at two different magnifications [5,000X & 20,000X] on a Scanning Electron Microscope of the surface "Before Ablation", shows two distinct features. The large "lumps" are from the coating underneath the Carbon containing layer, and will be described later. The fine granular features, as easily distinguished in the 20,000X view, are actually the carbon particles.

After Ablation, the debris left on the surface is the same as the larger ejecta seen on the previous slide. Again the carbon particles are clearly visible. This residue, held on the surface only by weak Van der Waals forces, has been transformed from its original water insoluble state to a completely water dispersible state. In the Dimension 400 platesetter, approximately 40% of the ablatable coating was left behind as debris on the plate; the remaining 60% was vaporized and captured by the filtration system.

After imaging, the debris can be easily removed by water or fountain solution. For color critical work, it is recommended that a simple water wash be used to prevent any carbon from contaminating the colored inks, especially yellow. For "Black Only" printing, the ANTHEM plate could go directly to press.

The photomicrographs of the surface after water washing show that carbon residue has been totally cleaned from the non-image area. This layer is completely hydrophilic.

HALFTONE DOT STRUCTURE:

Laser ablation imaging results in the typical line, text, and halftone dots common to lithographic plates. As seen in the optical micrographs shown in **Slide 6**, these dots appear as high contrast black, ink receptive images on the gray, water receptive background. **Slide 7a** shows an angled, low magnification [200X] view of balanced highlight and shadow dots on the Scanning Electron Microscope. In **Slide 7b**, at 500X, measurements are taken that show the dot diameters are equal to the expected value for the line screen that was chosen. In **Slide 8**, a higher magnification view [3,000X] on the SEM shows more detail of the ablated, hydrophilic area. The "grain" in the background appears as "nodules".

IMAGE AREA STRUCTURE:

To take a closer look at the structure of the highlight dot shown above, we can turn the plate on edge and slice the dot in half. Looking at the resultant cross-section at still higher magnification [25,000X] on the SEM, we can see the details of the multi-layered dot structure. **[Slide 9]**

At the bottom of the stack is standard litho-grade aluminum alloy. Next comes the columnar structure of the anodic layer of aluminum oxide. This layer has been treated to be hydrophilic. On top of that layer is the novel, hydrophilic Polymer-Ceramic composite layer approximately 1.5μ thick.

Embedded in the cross-linked polymer material are the hydrophilic ceramic nodules that gave rise to the "lumps" seen in **Slide 5 and Slide 8**. Above this section is the ablatable carbon layer, topped by a cross-linked oleophilic polymer layer.

Focusing on the uppermost layers at even higher magnification [100,000X] allows a close-up of the ablatable carbon layer, which is only 200 nm thick. The carbon particles, between 30-50 nm in diameter are clearly discernable. **[Slide 10]**

The high carbon to binder ratio results in a somewhat porous layer. This combination provides for an Infrared-absorbing structure with poor thermal conductivity, and the heat generated from the adsorption of the laser energy is concentrated in the carbon layer. As a result, the ablation efficiency is very high and the thermal spread [laterally and vertically] is extremely low. Therefore, resolution is not lost through dot spreading, and the damage to the polymer ceramic layer below is minimal.

The thickness of the carbon layer is roughly 200 nanometers [0.2 μ], and the polymer top layer is only about 50 nanometers. Thus, the total imaging and printing area thickness is approximately 0.25 μ. This is much thinner than the typical 1-2 μ coatings on conventional negative and positive working plates. Nevertheless, ANTHEM is capable of printing >100,000 impressions. Thinner layers, in general, allow for better resolution capability. Also, with ablation plates, or any other subtractive plate process, thinner coatings are desirable, because "the more you put on, the more you must take off".

The cross-linked polymer ceramic composite is tougher than the polymer alone would be. The nodules act as supports for the polymer film and even after 120,000 impressions at the gripper edge, the hydrophilic layer is still intact. As can be seen in **Slide 16** from 2,000X to 30,000X, even with significant polymer erosion and some nodule damage, the polymer is still adhering to the ceramic nodules and is still hydrophilic and not toning. The image layer at these conditions is still intact with only modest erosion of the 1% dots at 175 lpi.

All the organic layers on the ANTHEM plate have been thermally cross-linked in manufacturing; therefore no pre-baking or post-baking is necessary. This also results in layers that are water and solvent insoluble, so that ink solvents, monomers in UV ink, and wash-up solvents will not harm the plate.

NON-IMAGE AREA STRUCTURE:

Viewing a cross-section of the non-image area on the SEM at 30,000X [**Slide 11**] shows a close-up of the poly-ceramic layer on the anodic layer. The surface of the polymer shows no trace of any carbon debris after water washing. The large ceramic nodule observed gives a hint at what appears to be a fine structure. Also evident, between the poly-ceramic layer and the anodic layer, is an interfacial layer that formed as a result of a reaction with the silicated aluminum oxide surface. This gives the polymer-ceramic layer excellent adhesion to the anodic surface.

Although the presence of the ceramic nodules provides the polymer layer with a topography that mimics the graining of aluminum, the surface has a relatively low surface roughness [Ra] in comparison. This can be seen in the surface view shown at relatively low magnification [2,000X] in **Slide 12**.

However, this novel hydrophilic surface allows for the carrying of a relatively low wet film thickness of fountain solution on press. This then allows for maintaining a relatively thin ink film for proper ink / water balance. This thin ink film can result in sharper images at higher densities than would be expected. With less water being carried, there is less water emulsification into the ink. Therefore, the thinner ink film can actually have a higher pigment load. This will result in higher density and higher gloss images.

Smooth plate surfaces in the past have often lead to narrow ink/water balance on press. Fountain solution could easily evaporate at high speeds and lead to toning. The poly-ceramic layer does not exhibit this behavior. To understand why this is possible, a closer examination of the ceramic nodules is required.

In **Slide 13** we have an unimpeded view of the ceramic nodules at 10,000X after the polymer layer has been stripped. It can clearly be seen that the nodules are spheroidal in shape, with many having one or more "craters" in evidence. The particle size distribution is centered between 0.5 and 1.5 μ in diameter. These craters are created during the formation of the ceramic nodule by gas evolution and add to the overall surface area of the nodules.

These ceramic nodules are formed inside the polymer layer through phase separation and are simultaneous to the cross-linking reaction of the polymer. They start as 3-7 nm gels that coalesce into the larger nodules consisting primarily of hydrous zirconium oxide.

With a 100,000X close-up of a single nodule, a definite porosity on the surface of the ceramic is observed in **Slide 14.** The closer examination of a single crater in **Slide 15** at 200,000X indicates the nanoporous structure of this hydrophilic ceramic.

The combination of the partially permeable polymer and the inclusion of the "rock sponge" nodules apparently result in a capability to provide a self-modulating reservoir of fountain solution that widens the press latitude of this low Ra surface. This is done while taking advantage of the fact that this surface does not provide the opportunity to trap ink particles within the torturous surfaces that result from the electrochemically etched or slurry grained anodized surfaces that are typical of standard plates. Thus the tendency for toning is reduced with the poly-ceramic layer.

In order to take advantage of this behavior, it is recommended that during roll-up on press, the plate surface be allowed to run with fountain solution for 10-15 seconds before dropping the ink. This allows time for the poly-ceramic layer to imbibe the fountain solution. This will allow for the fastest roll-up and the highest paper savings.

Another advantage of this novel hydrophilic surface is that no gumming is required before going to press. The polymer ceramic composite layer provides all the benefits of a gum layer in protecting the non-image layer and is more permanent. No limitations are observed on the amount of time between ablation imaging, "washing" the plate and roll-up on the press. The plate can be imaged and washed at once, or one month later. It can be mounted on press and printed immediately after "washing", or one month later without deterioration in printing results. Not having gum placed on top of the ink receptive layer also assists with a rapid roll-up to reach full density, since no gum blinding can occur.

PRINTING PERFORMANCE:

The results of this unique surface on roll-up can be seen in **Slide 16** where the density build-up of image is plotted versus number of impressions. As is clearly indicated, acceptable print quality is achieved prior to 10 impressions for Black ink. [Flint ink, Varn fountain solution, Sakurai press, Day blanket, Sappi paper]

This was done with four different lots of plate, from 3 months to 12 months in age, all imaged at the same time. Roll-up and "dot quality" are all comparable. The same behavior was seen for all colors. The Magenta graph is shown in **Slide 17**. This behavior is independent of ink film thickness and density as shown in **Slide 18**.

A summary of product performance that results from the use of this novel polymer-ceramic composite layer in the ANTHEM Thermal CtP plate structure is given in **Slide 20**.

Of particular note, is the performance with UV inks. Those inks are notorious for toning, due to the more polar nature of the ink; and the tendency for short run length, due to the attack on the image polymer by the monomers in the UV ink and the solvents used to clean the plate. This behavior is not observed with the polymer-ceramic composite surface structure of the ANTHEM plate.

Similarly, the novel hydrophilic surface is ideally suited to working with the polar, non-aqueous dampening fluid found in the "single fluid ink" demonstrated by Flint at DRUPA.

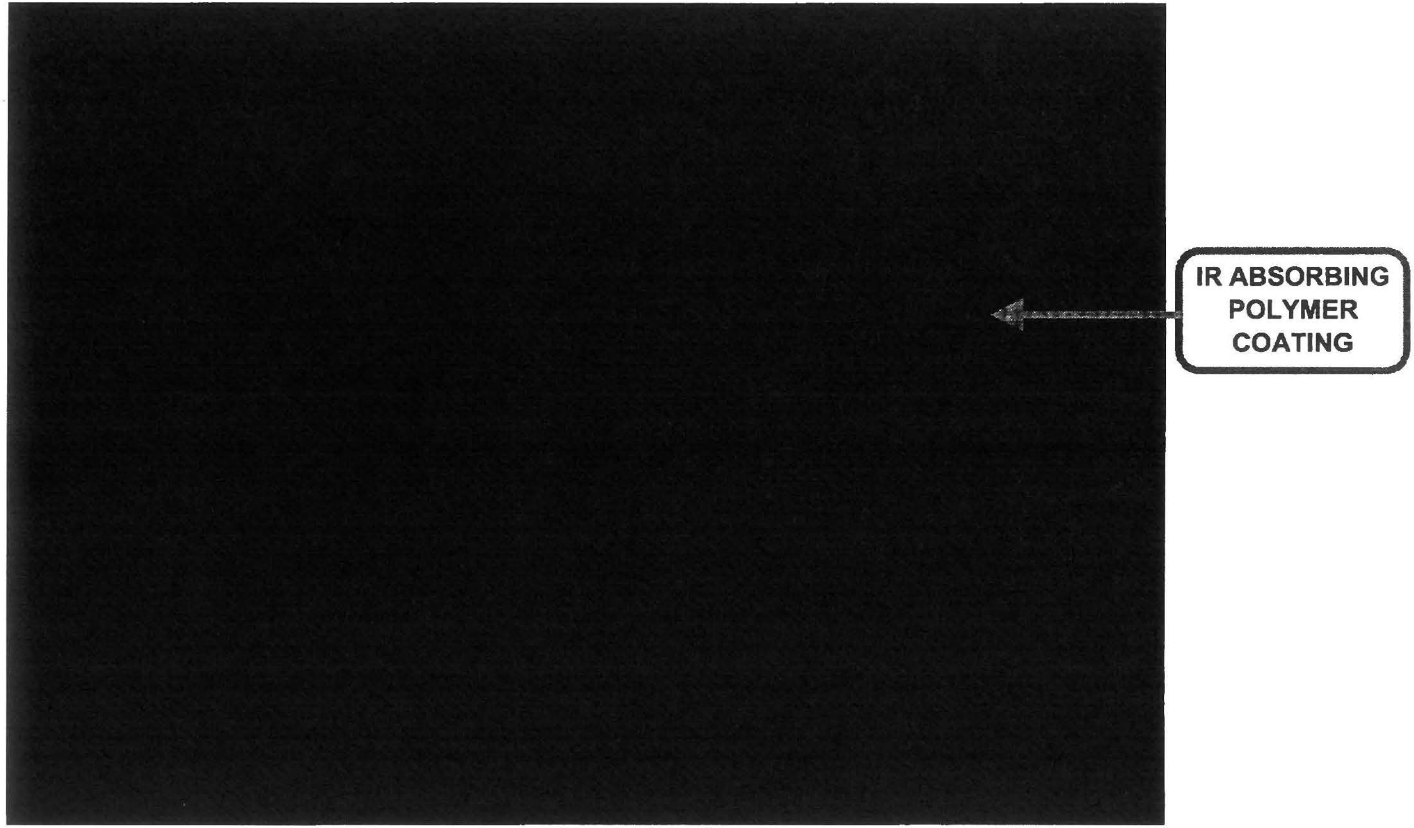
CONCLUSION:

A novel polymer-ceramic hydrophilic surface, contained within the structure of the ANTHEM thermal CtP product, allows this plate to:

(1) be imaged by thermal ablation
(2) be processed by a simple water wash
(3) need no gumming
(4) roll-up cleanly and rapidly on press
(5) demonstrate unexpected ink / water balance and latitude
(6) demonstrate similar behavior with unconventional inks [UV & SFI]
(7) need no special fountain solutions or additives to obtain this performance

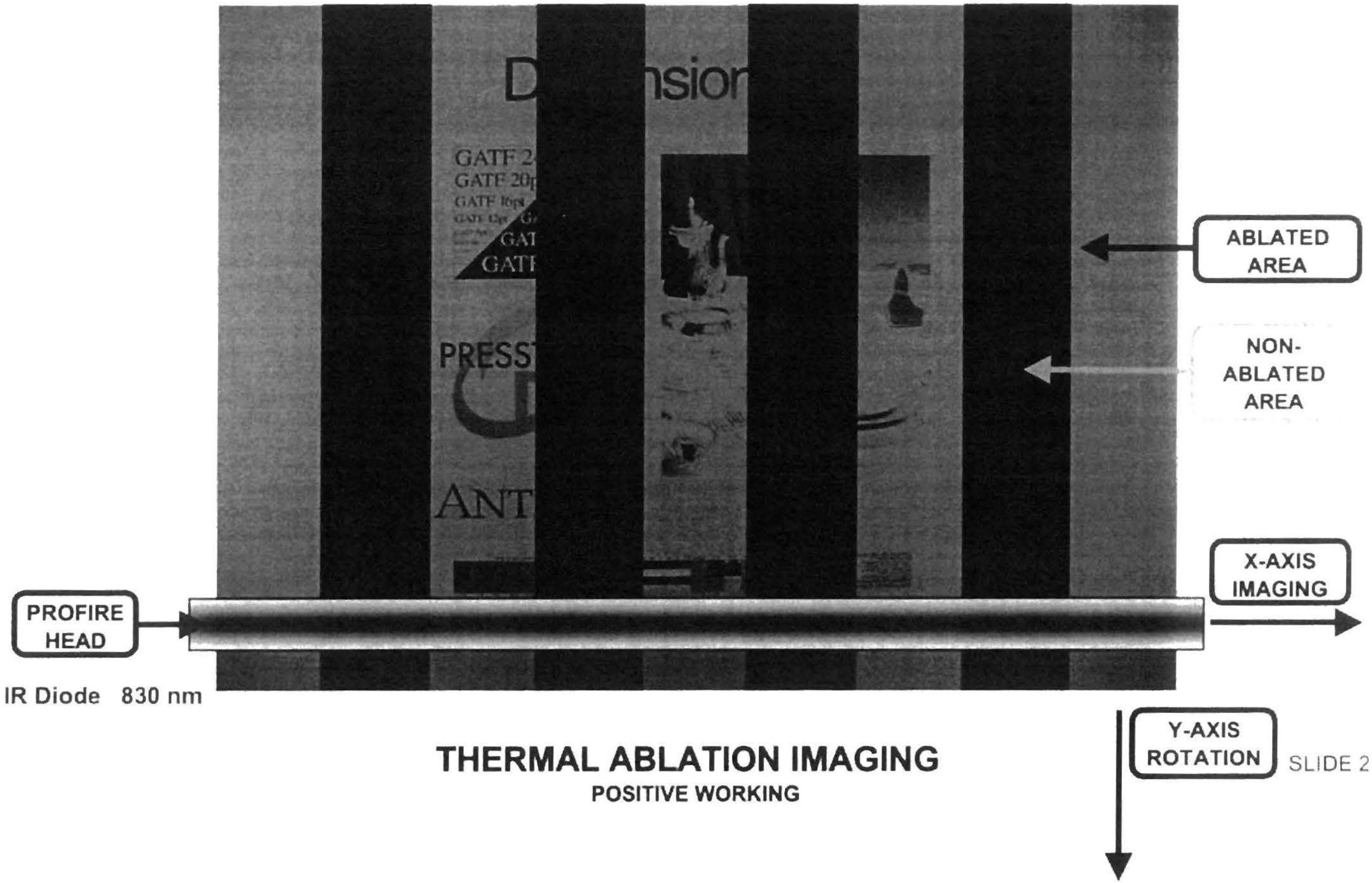
This technology represents the advances in materials that will be necessary to provide printers with simpler, non-chemical processing for CtP applications.

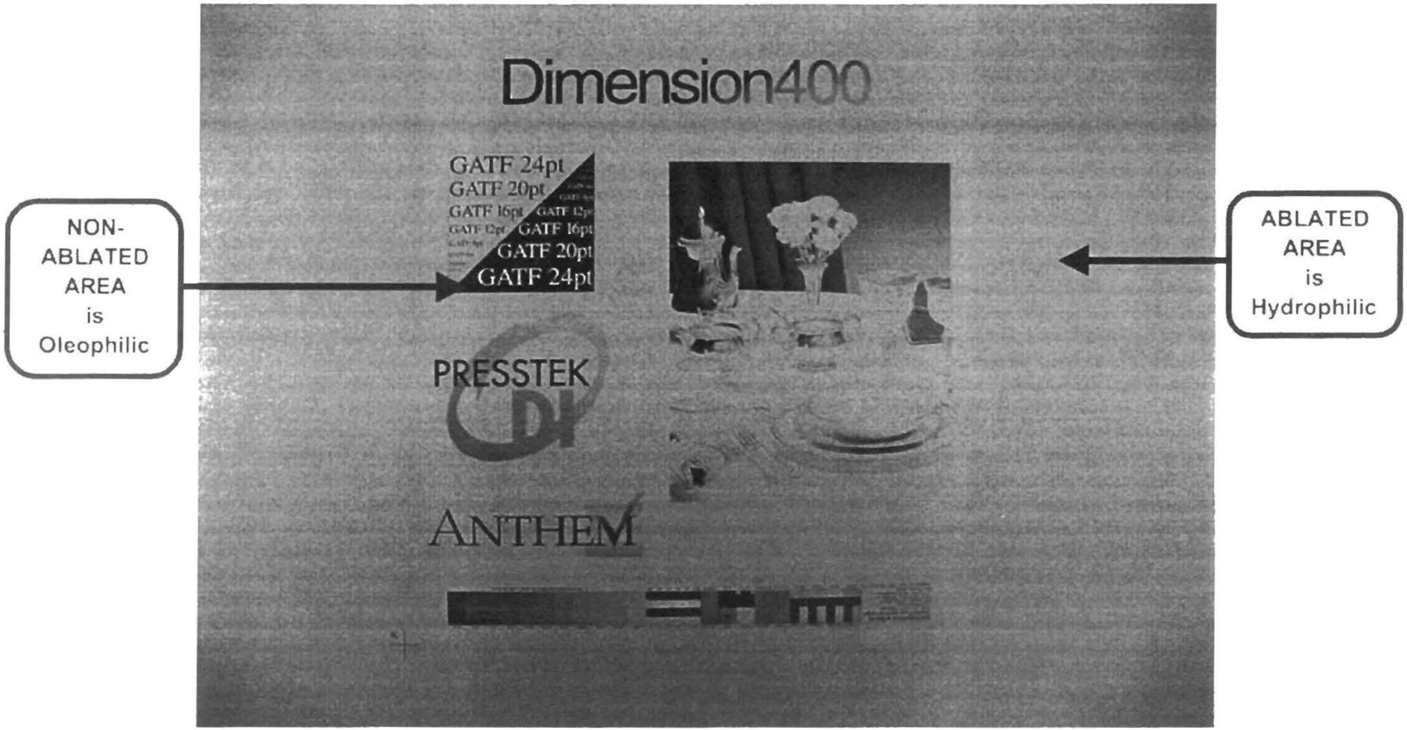
TAGA 2001



UNIMAGED PLATE

SLIDE 1


ABLATED AREA
NON-ABLATED AREA
X-AXIS IMAGING
PROFIRE HEAD
IR Diode 830 nm
Y-AXIS ROTATION
THERMAL ABLATION IMAGING
POSITIVE WORKING
SLIDE 2

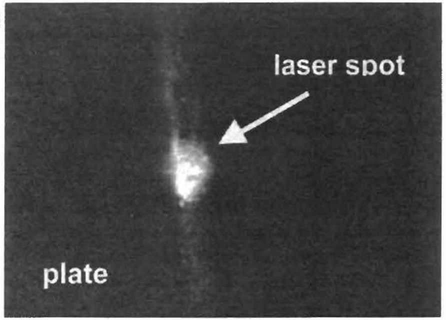


IMAGED PLATE
POSITIVE WORKING

SLIDE 3

ANTHEM Laser Ablation Imaging Event

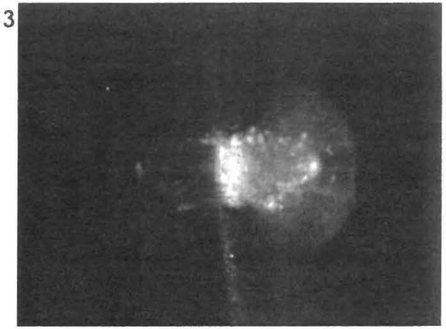
110 ns pulse, 35μ spot **4000X**

1


t = 20 ns

2

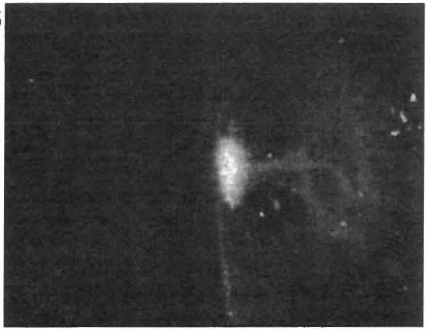

t = 80 ns

3


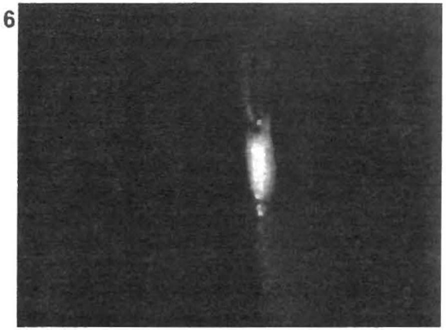
t = 220 ns

4


t = 510 ns

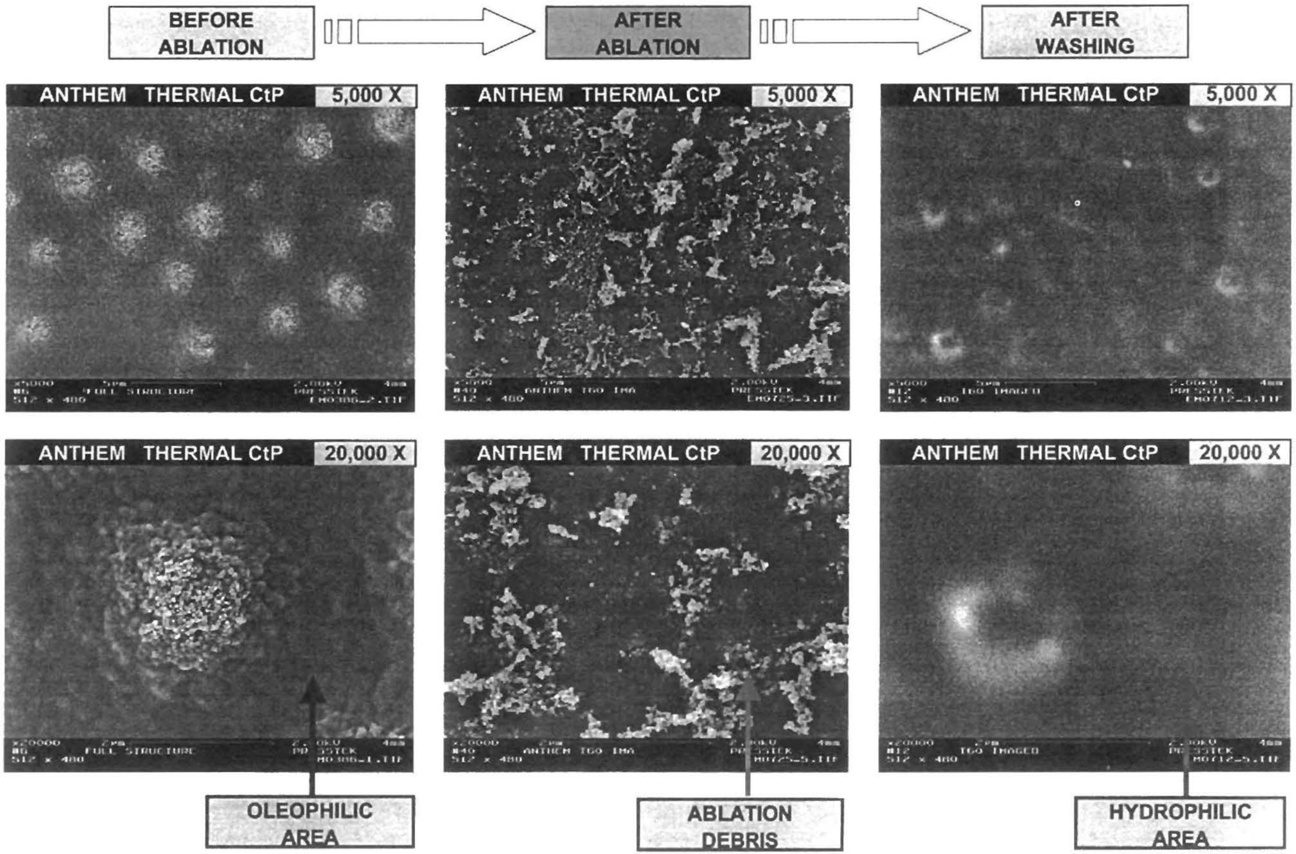
5


t = 850 ns

6


t = 1 μsec

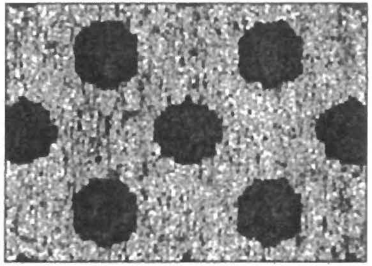
SLIDE 4


BEFORE ABLATION
AFTER ABLATION
AFTER WASHING
ANTHEM THERMAL CtP
5,000 X
ANTHEM THERMAL CtP
5,000 X
ANTHEM THERMAL CtP
5,000 X
ANTHEM THERMAL CtP
20,000 X
ANTHEM THERMAL CtP
20,000 X
ANTHEM THERMAL CtP
20,000 X
OLEOPHILIC AREA
ABLATION DEBRIS
HYDROPHILIC AREA

SLIDE 5

Optical Microscope Photographs of ANTHEM CtP Images

ANTHEM / DIMENSION 400



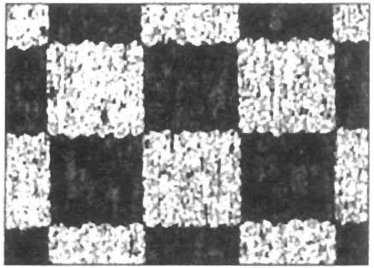
175 lpi 25% Dots @ 200X

2540 dpi 100dpmm

Pulse Width: 3.2µs

Spot Size: 20µm

ANTHEM / PEARLsetter-74



150 lpi 50% Dots @ 200X

1270 dpi 50dpmm

Pulse Width: 4.5µs

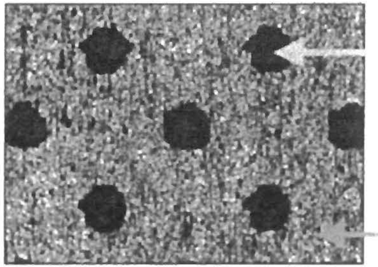
Spot Size: 35µm

ANTHEM

Positive Working

Thermal Ablative

CtP



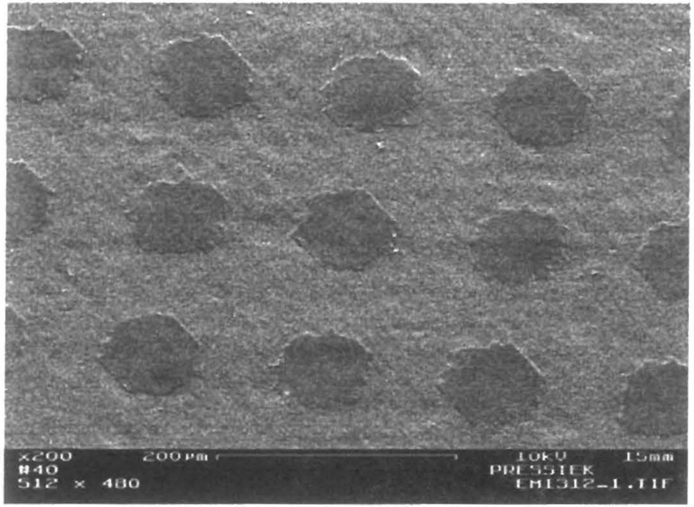
Ink Receptive
Non-Ablated Area

Water Receptive
Ablated Area

175 lpi 10% Dots @ 200X

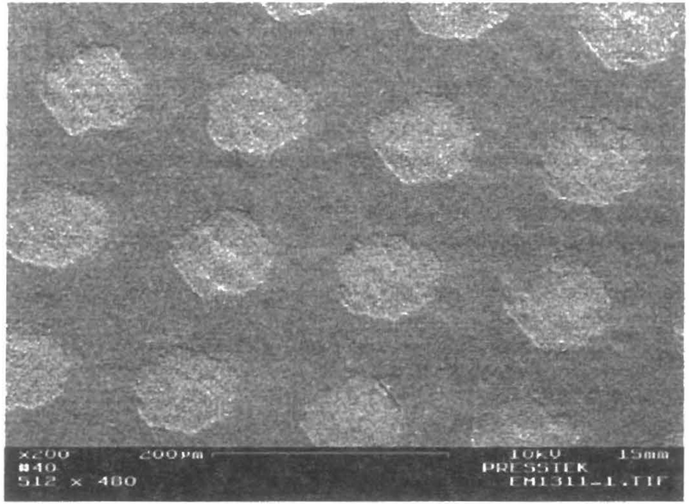
SEM MICRO-PHOTOGRAPHS of ANTHEM CtP ABLATION IMAGES

ANTHEM Highlight Dot



25% 175lpi 30° 200 X

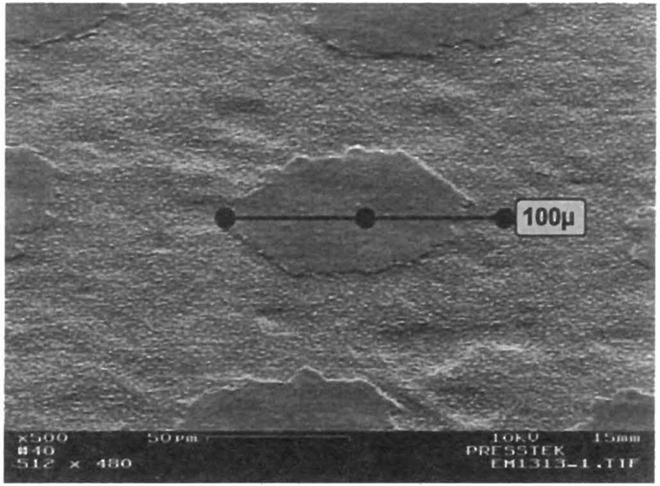
ANTHEM Shadow Dot

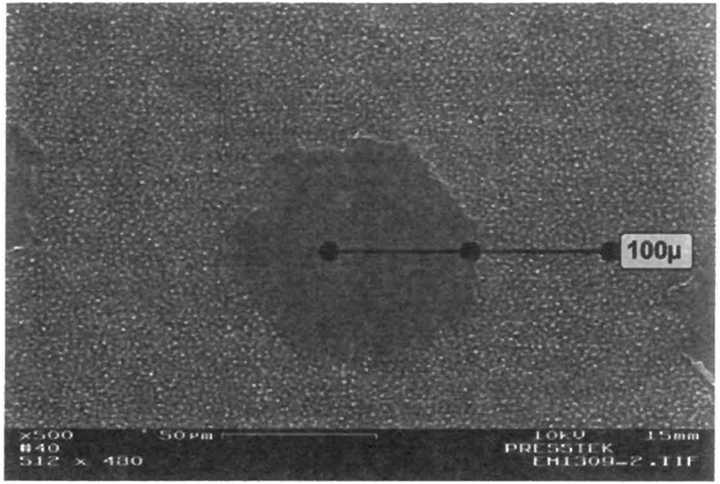


75% 175lpi 30° 200 X

SLIDE 7a

SEM MICRO-PHOTOGRAPHS of ANTHEM CtP HIGHLIGHT DOTS



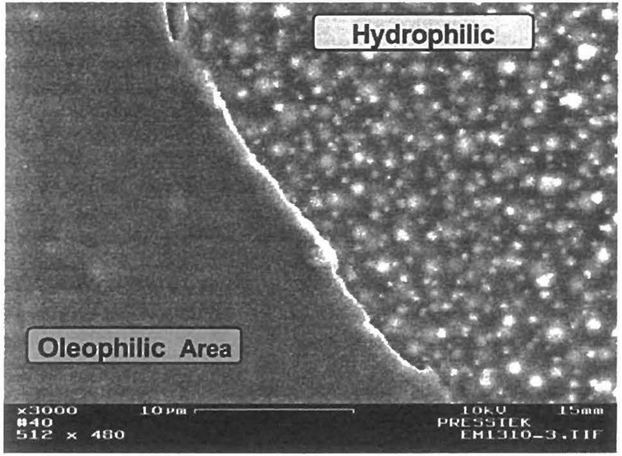


60° Tilt	**500 X Magnification**	**0° Tilt**	**500 X Magnification**
25% Dot	**175 lpi 2540 dpmm**	**25% Dot**	**175 lpi 2540 dpmm**
	D = 82µ		**D = 82µ**

SLIDE 7b

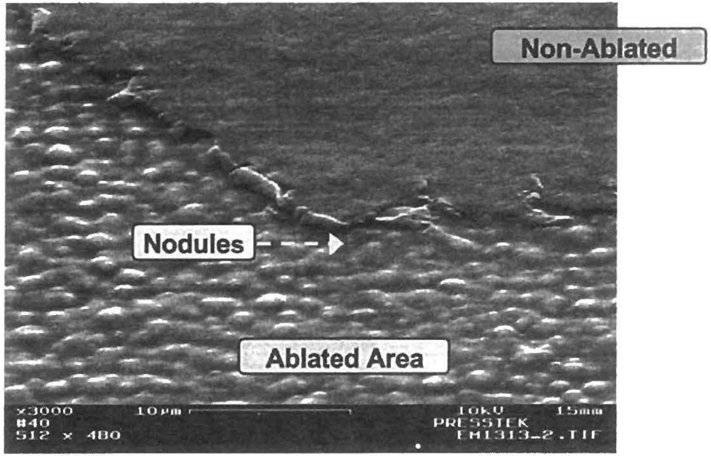
SEM MICRO-PHOTOGRAPHS of ANTHEM CtP IMAGED DOTS

ANTHEM Shadow Dot



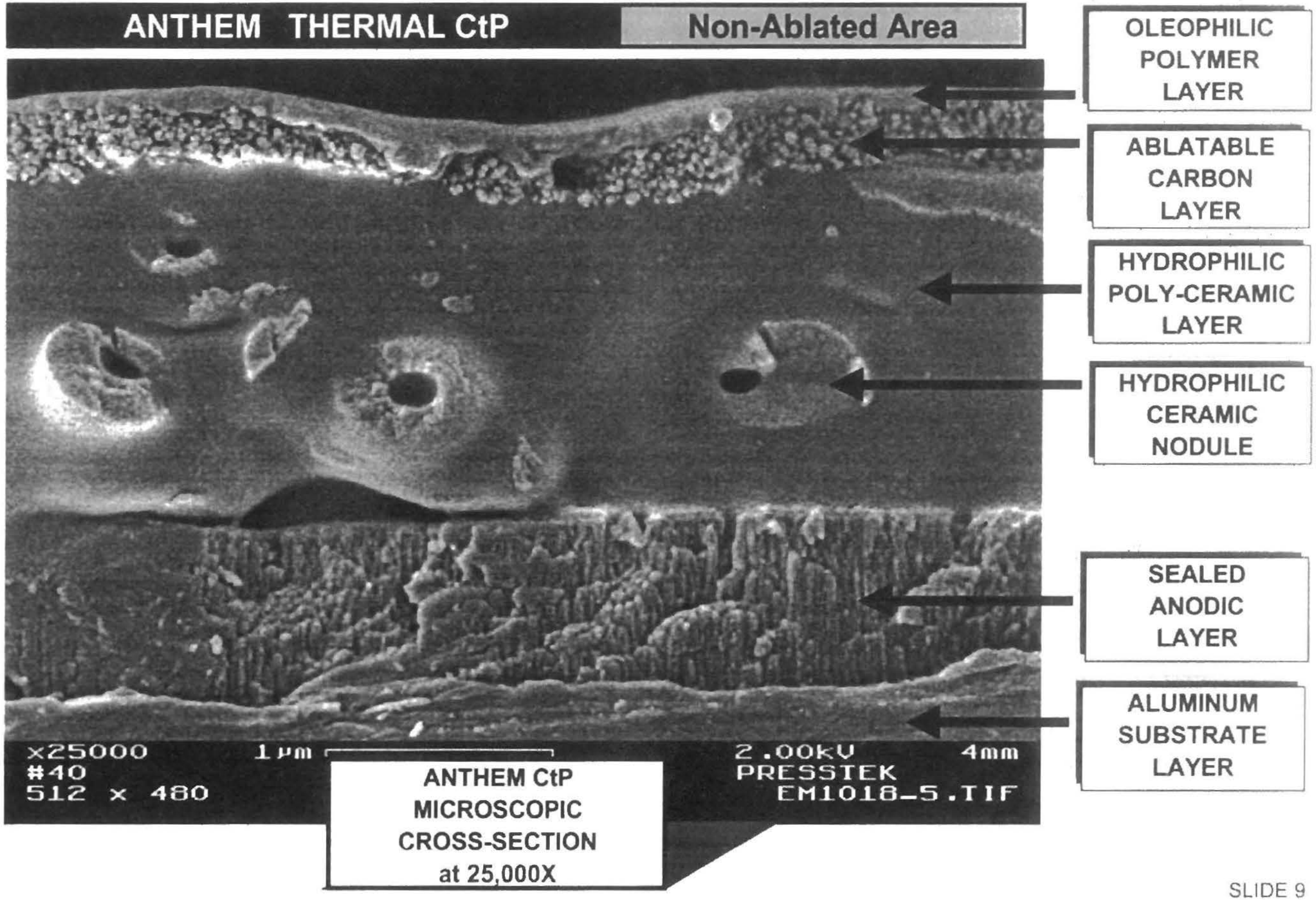
75% 175lpi 0° 3,000 X

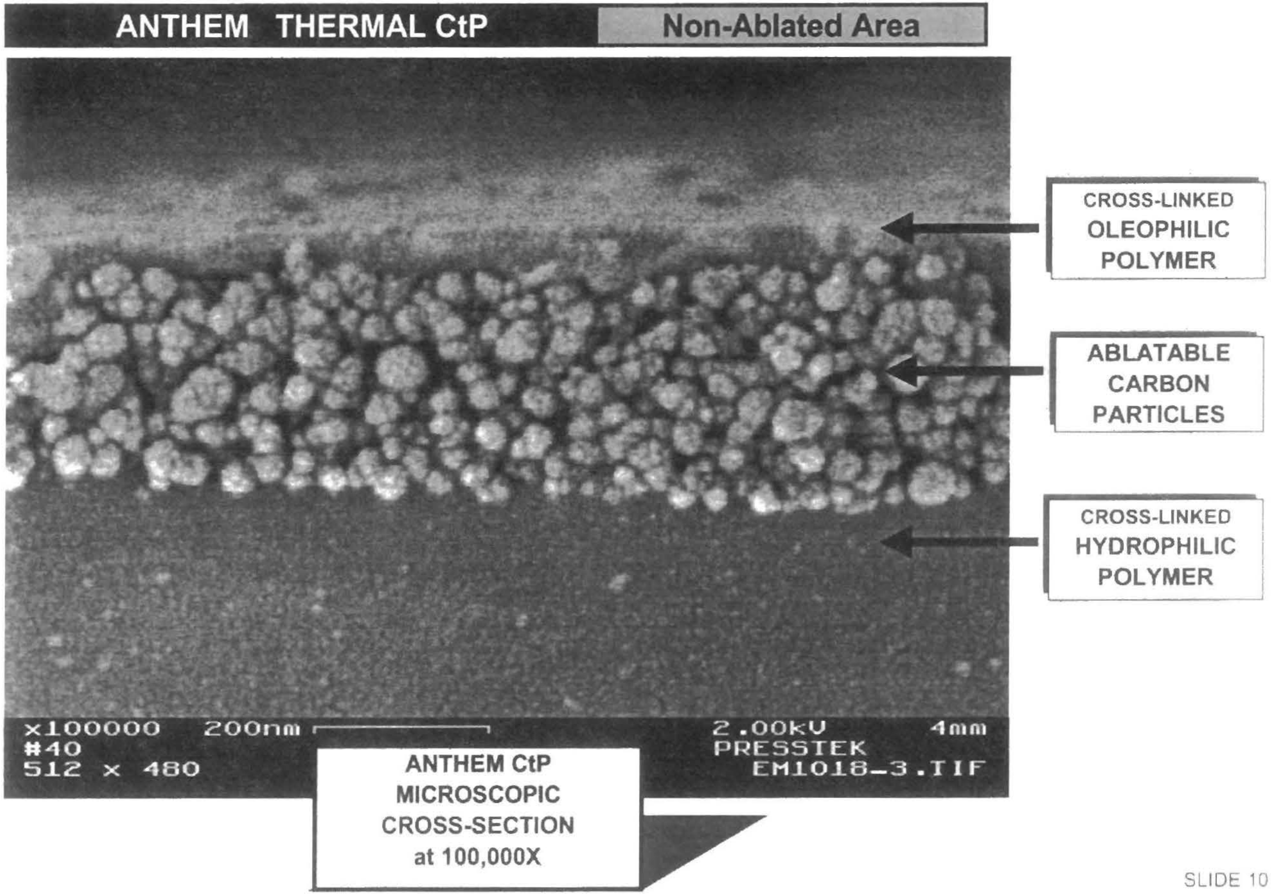
ANTHEM Highlight Dot

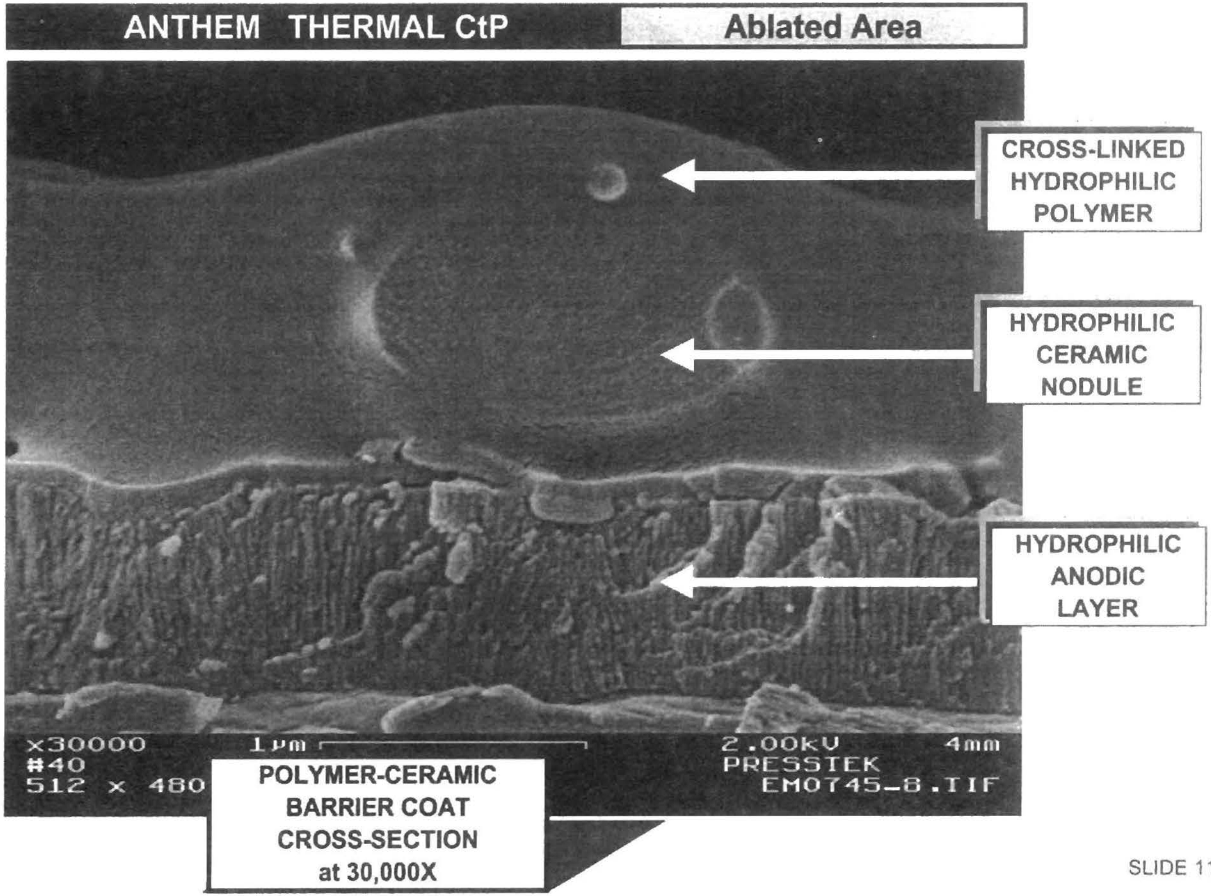


25% 175lpi 60° 3,000 X

SLIDE 8

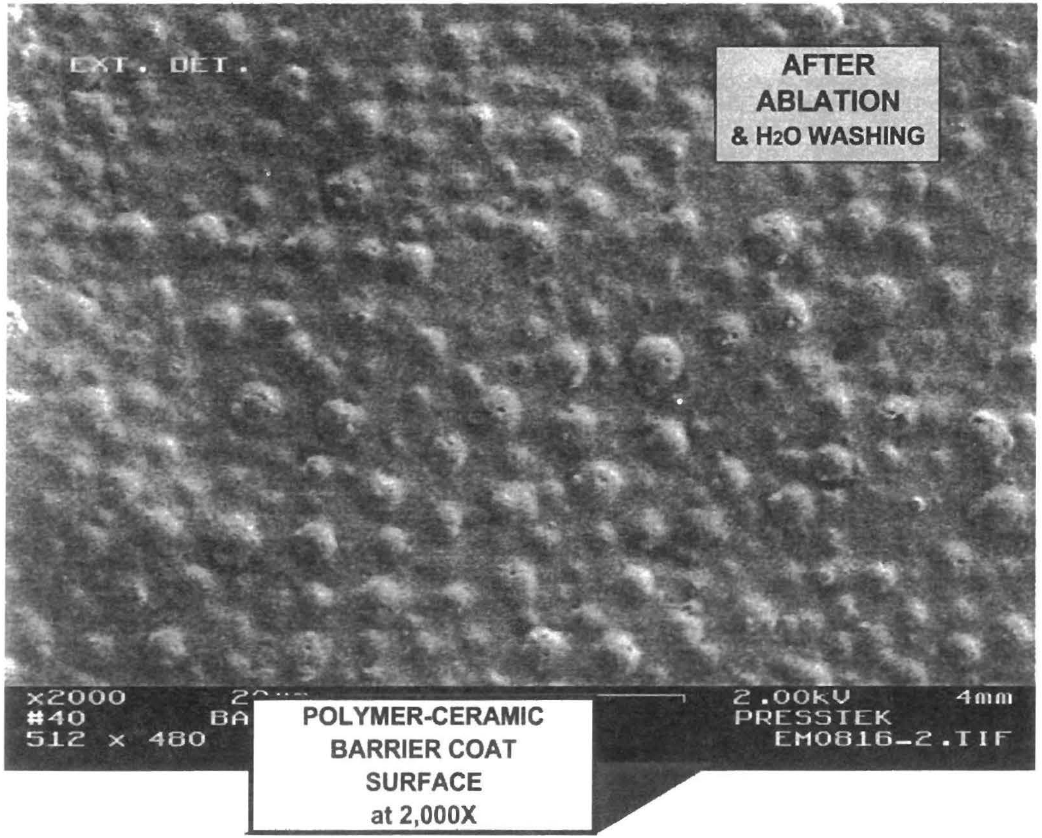

ANTHEM THERMAL CtP
Non-Ablated Area
OLEOPHILIC POLYMER LAYER
ABLATABLE CARBON LAYER
HYDROPHILIC POLY-CERAMIC LAYER
HYDROPHILIC CERAMIC NODULE
SEALED ANODIC LAYER
ALUMINUM SUBSTRATE LAYER
x25000 1 µm
#40
512 x 480
2.00kV 4mm
PRESSTEK
EM1018_5.TIF
ANTHEM CtP MICROSCOPIC CROSS-SECTION at 25,000X


ANTHEM THERMAL CtP
Non-Ablated Area
CROSS-LINKED OLEOPHILIC POLYMER
ABLATABLE CARBON PARTICLES
CROSS-LINKED HYDROPHILIC POLYMER
x100000 200nm
#40
512 x 480
2.00kV 4mm
PRESSTEK
EM1018-3.TIF
ANTHEM CtP MICROSCOPIC CROSS-SECTION at 100,000X
SLIDE 10


ANTHEM THERMAL CtP
Ablated Area
CROSS-LINKED HYDROPHILIC POLYMER
HYDROPHILIC CERAMIC NODULE
HYDROPHILIC ANODIC LAYER
x30000
#40
512 x 480
1μm
2.00kV
4mm
PRESSTEK
EM0745_8.TIF
POLYMER-CERAMIC BARRIER COAT CROSS-SECTION at 30,000X

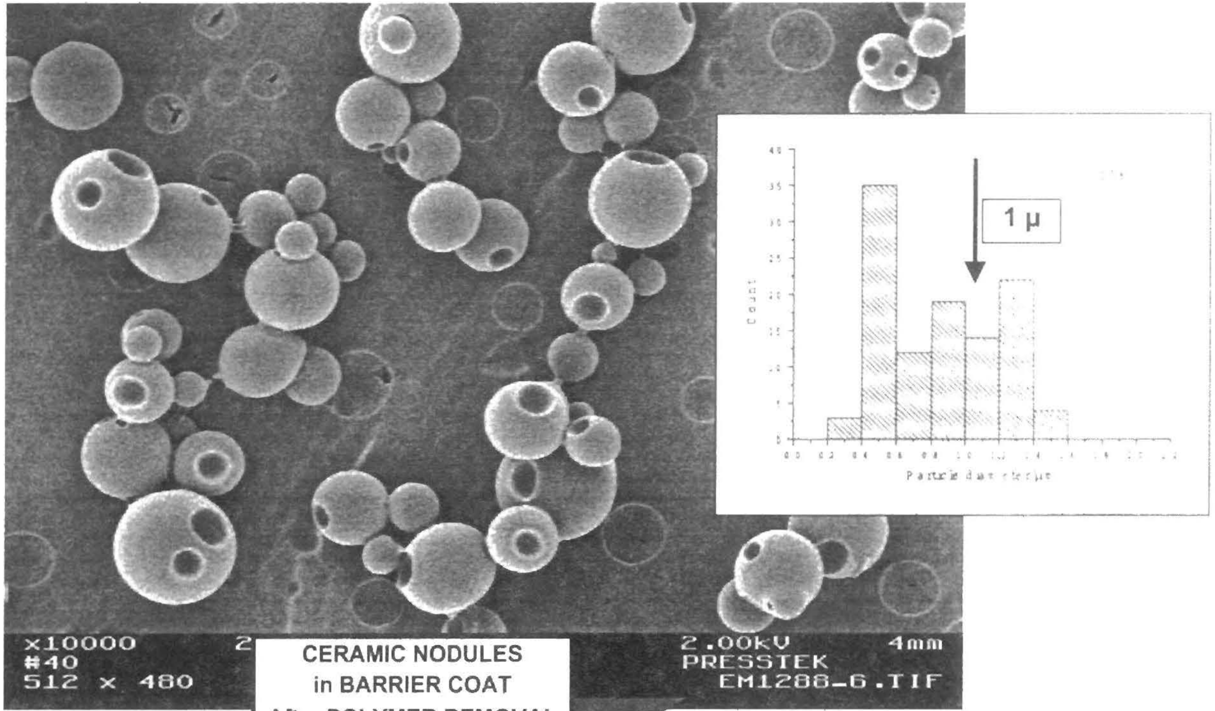
SLIDE 11

ANTHEM THERMAL CtP — Hydrophilic Surface



NOVEL HYDROPHILIC LITHOGRAPHIC SURFACE for THERMAL CtP

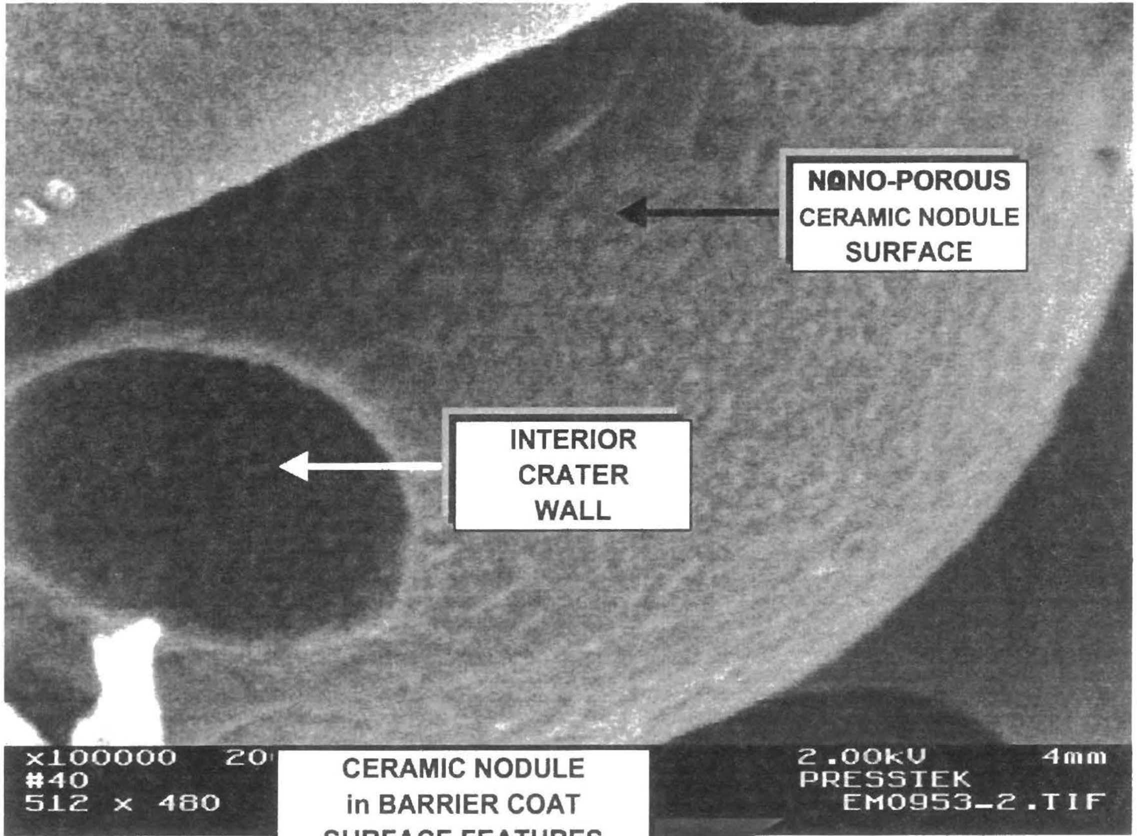
ANTHEM THERMAL CtP — Ceramic Nodules



SLIDE 13

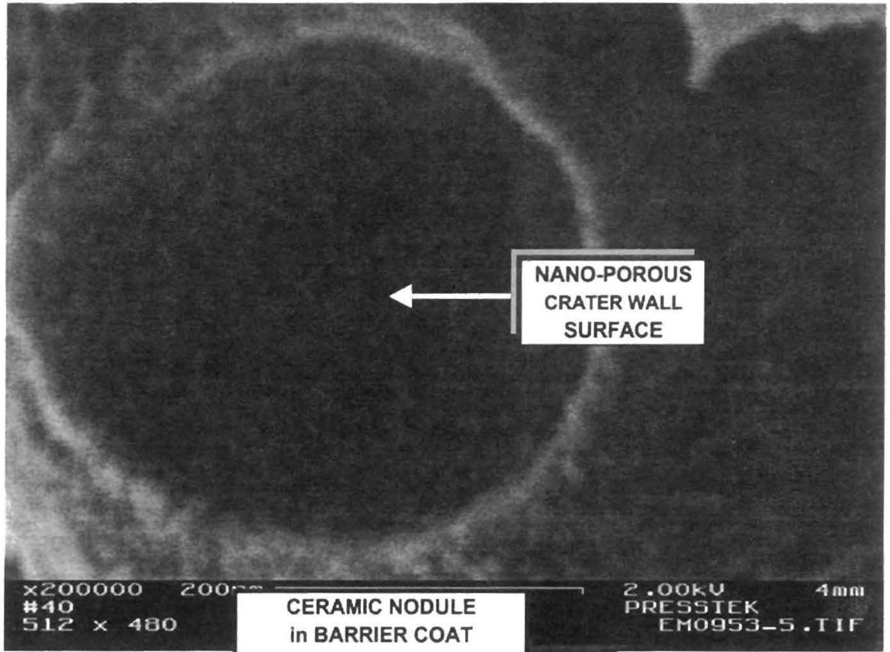
ANTHEM THERMAL CtP Ceramic Nodule

547



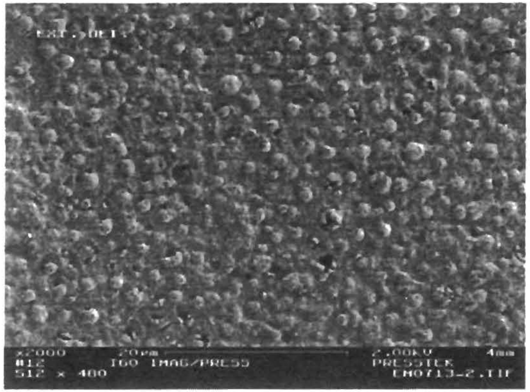
CERAMIC NODULE
in BARRIER COAT
SURFACE FEATURES
at 100,000X

ANTHEM THERMAL CtP | Ceramic Nodule

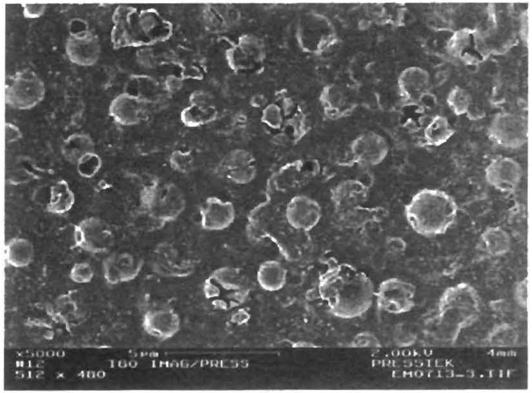


CERAMIC NODULE
in BARRIER COAT
CRATER WALL SURFACE
at 200,000X

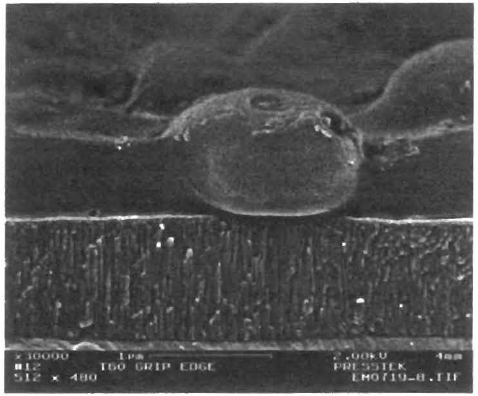
ANTHEM CtP "Polymer-Ceramic Layer" / Non-Image Area after 120,000 Impressions



2,000X

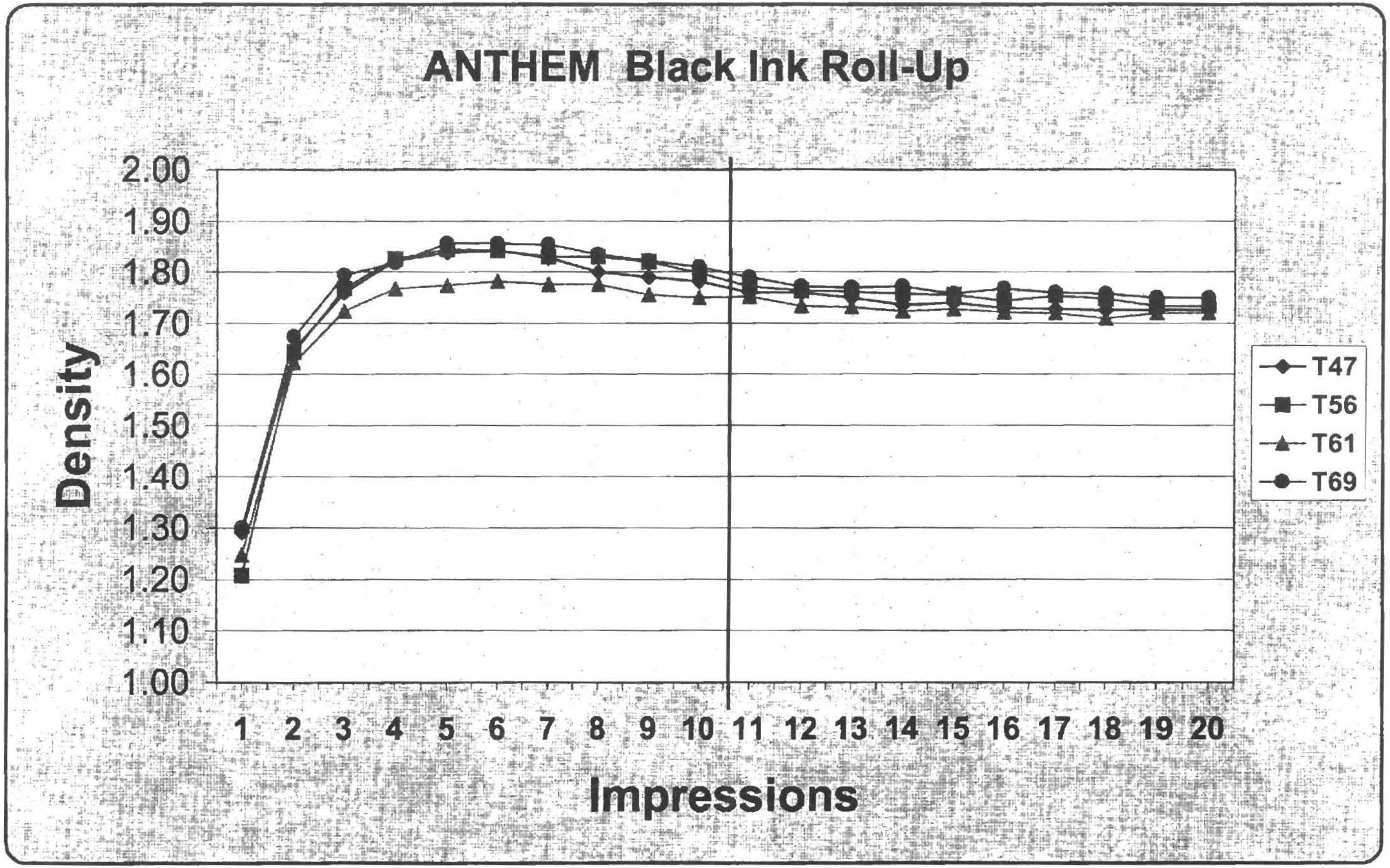


5,000X



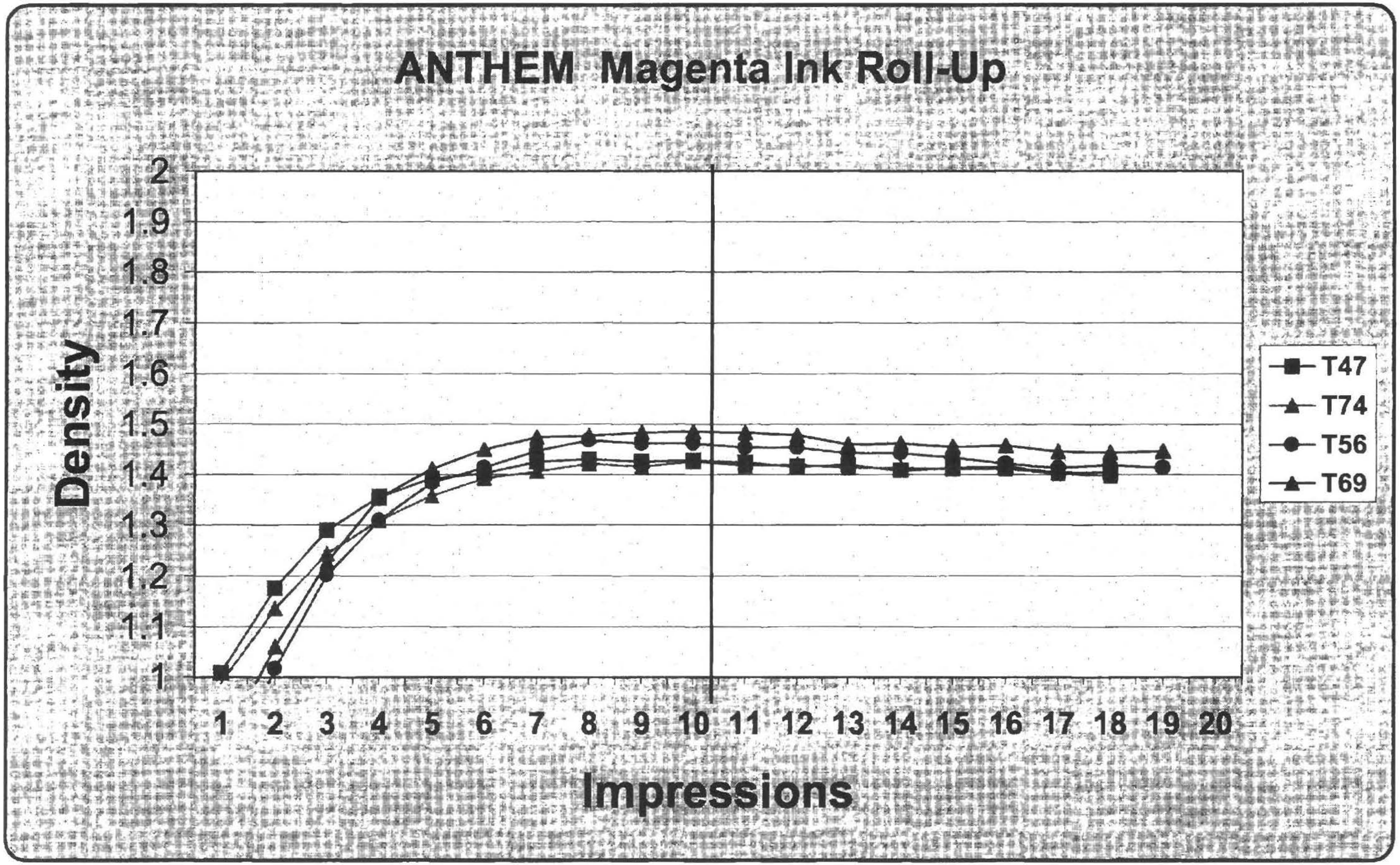
30,000 X Cross-section

SLIDE 16



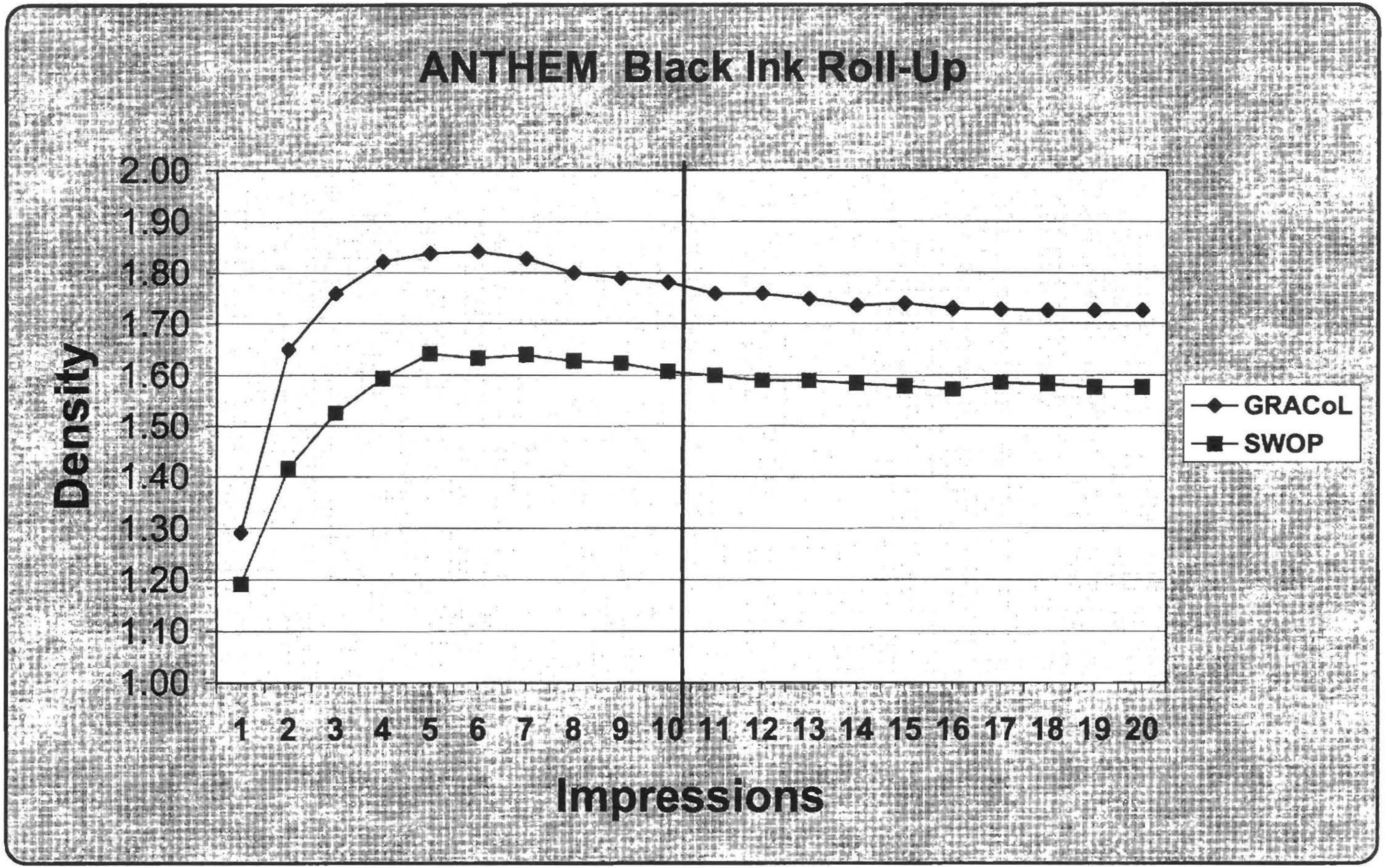
FLINT INK VARN FOUNTAIN SAKURAI PRESS DAY BLANKET SAPPI PAPER

SLIDE 17



ANTHEM Magenta Ink Roll-Up
Density
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Impressions
T47
T74
T56
T69

SLIDE 18


ANTHEM Black Ink Roll-Up
Density
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Impressions
GRACoL
SWOP

SLIDE 19

POSITIVE WORKING CtP

- NON-PHOTOSENSITIVE
- HIGH RESOLUTION - - 200 lpi+
- WATER WASH for COLOR
- NO GUMMING NEEDED
- RAPID ROLL-UP <10 Sheets
- RAPID RESTART <5 Sheets
- RESISTANT to SOLVENTS
- ENHANCED SFI PERFORMANCE

THERMAL ABLATION IMAGING

- STABLE SHELF-LIFE 2 Yrs. +
- RUN LENGTH - - 100,000+
- NO-PROCESS for BLACK
- NO BAKING NEEDED
- INK / WATER BALANCE LATITUDE
- LESS FOUNTAIN NEEDED
- LESS INK / HIGHER DENSITY
- SUPERIOR UV INK PERFORMANCE

SLIDE 20