

The Ink Cure Analyzer^ä

Degree of Polymerization Testing Instrument



From:

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Ink Cure Analysis

Your Con-Trol-Cure Ink Cure Analyzer is one of the only instrumental methods for determining the degree of cure for an ink or coating. The method is valid and applicable for many types of coatings and inks including thermally cured, oxidatively cured, and radiation cured. With a little care this method can yield reliable reproducible data. Following are some tips to help you become well versed in Ink Cure Analysis technique and interpretation.

SOME COMMENTS AND CONCEPTS.

ICA is a comparative form of analysis. Unlike a thermometer or balance, the data you will generate with this method must be interpreted in context. This means that a given test result must be compared to some known point of reference. Such a reference or standard is quickly and easily generated with your specific ink or coating, for instance by generating ICA data for a series of samples in a cure ladder. Once this has been accomplished it is straightforward to see where in the cure continuum your particular sample lies. There are many other analytical methods such as chromatography, spectroscopy, etc. which compare an unknown to some pre-established standard.

HOW DOES ICA WORK?

The concept which Ink Cure Analysis rests on is simple to understand. A coating which is poorly crosslinked will be swelled to a greater degree than one which is well crosslinked. When we use the term "swell" to describe the interaction between a polymer and a solvent we refer to the tendency for a polymer to absorb solvent and to increase, however imperceptibly, in size. A sponge will absorb water and swell; on the molecular level the action between polymer and a compatible solvent is much the same. The specially formulated MSS solutions consist of a low boiling solvent (one which will evaporate quickly), and one part in 100,000 Carbon-14 containing compound. In an ICA test, 17uL is deposited on the surface of the ink or coating to be tested, swells the film to a greater or lesser extent, and allows the C-14 tagged material to enter the film surface. The solution on the surface will quickly evaporate leaving only the material which was able to penetrate. The ICA detection system consists of a Geiger-Mueller counter interfaced with a computer. During data collection solvent molecules are counted at the film surface by virtue of the C-14. The profile generated by the C-14 is indicative of how the film behaves in the presence of the solvent.

In each test data is collected for 180 seconds, a plot of C-14 counts Vs time is generated, and four cure indices are calculated. These are explained later. A full understanding of the mathematics behind these calculations is not necessary to obtain useful information by ICA. This test data is then stored in a computer file for later analysis or comparison. Such stored data can be printed out, copied to diskette, or retrieved for comparison with more recent tests. The filing system will be more fully described in a section addressing the ICA software.

SOLVENTS, C-14 AND SAFETY:

Many of the MSS solutions are based on halogenated solvents such as carbon tetrachloride, methylene chloride, trichlorotrifluoroethane, etc. These are common materials with many industrial uses. As with all solvents they should be used with due care. One should avoid skin contact: wear rubber gloves when transferring solution from ampules to vials. If Skin contact does occur wash the exposed area with soap and water. In Ink Cure Analysis one will never need to handle more than a few ml at a time. Carbon 14 is a safe radiochemical which has many uses in industry. This isotope of carbon emits a Beta particle, which is an electron. This is considered "soft" radiation as it cannot penetrate glass, paper, skin, etc. One could perform ICA every day for years and still not receive the same dose of radiation experienced in a single X-Ray. Radiochemicals are under the close supervision of the Nuclear Regulatory Agency. Because of the exceedingly small concentration and the innocuous nature of radiation found in MSS Solutions, they are exempted under USNRC 49 CFR 173-421.

INK CURE ANALYSIS EXPERIMENTAL TECHNIQUE.

To obtain best results one is advised to develop a consistent experimental procedure. Some very simple practices will help ensure that your results are accurate and reproducible. A: Test Solution Handling: While the solutions are meant to evaporate quickly from the film surface, described as having "high vapor pressure", the C-14 containing material evaporates slowly because of its low vapor pressure. Left uncovered the high vapor pressure solvent will evaporate preferentially causing the concentration of C-14 to increase. Hence, if one ran tests for a period of time with an open vial of solution, the total counts during a test would slowly increase as the solvent evaporated.

The curve profile would remain the same but the number of C-14 molecules detected in 17 μ L would become higher, as would the reported "total counts". The Solution Handling System, with its special Insertable Closure, was developed for this reason: to keep the high vapor pressure solvent from evaporating too quickly.

Important Tip: You should always transfer solution to a re-sealable vial after opening a new ampule, and use the white Insertable Closure on the vial you are using presently. Cover that vial with its black Teflon lined cap when done for the day.

As with any analytical method the proper handling and selection of sample materials is necessary for best results. A specimen which is about the size of a quarter is required to completely cover the sample stage. One should avoid undue contact: this method is sensitive enough to be skewed by fingerprints. To characterize a given ink or coating solid areas of coverage are best. ICA can certainly be conducted on pattern printed areas, but sample to sample variation is more likely to occur.

In the beginning some practice may be required to deposit test solution in the desired location without splattering, to move the detector head into place and to begin data collection, but most are able to conduct the test with confidence in a short period of time.

It does take some finite period of time to deposit the solution, to put the detector in place and to begin collecting data; does this influence the outcome? A typical curve begins with a sharp peak as the surface solvent evaporates. This occurs between 10 and 30 seconds into data collection. The upper point of this peak is important in the MSS Index calculations which compare the region of high counts to the region of lower counts, or the beginning of the test to the end in some mathematical fashion. Keep in mind that one data point is plotted every nine seconds. In a typical curve the apex is the fourth point which is 27 seconds into the test. With a little practice one can deposit the solution put the detector in place and begin data selection in about 5 seconds. The crucial information which is obtained at the peak of the curve is in no danger of being lost.

MSS-TEST SOLUTIONS; WHAT ARE THEY, WHICH ONE SHOULD I USE?

An entirely new series of MSS Test Solutions are currently available to replace the older MSS Blue, Red and Yellow solutions, which were all based on trichlorotrifluoro ethane. Because they contained trace amounts of Freon these older solutions are no longer available (as of 01/01/1996).

The new families of solutions are described by their components, such as: BWxxH, BKxxP, and BV. The "B" in all of the above is one part per 100,000 of Tridecane-C14, the active testing agent. The "xx" between the primary and secondary solvents indicates the strength of the secondary solvent (05,10,20, or 40), where increasing numbers indicate higher concentrations, and therefore a potentially higher degree of invasiveness into the coating being tested. The remaining compounds are the primary and secondary solvents used to facilitate the infiltration of the C14 into the coatings being tested and tend to work best in pairs.

For most acrylic or urethane type inks or coatings, BW20H has the proper degree of solvency; for most epoxy based coatings, BK10P has the proper degree of solvency, and for some coatings having very light crosslinking properties, BV may be able to distinguish small differences in crosslink density. The "W" is 2,3-DimethylButane, and is usually paired with "H", Methylene Chloride. The "K" is Cyclopentane, and is usually paired with "P", TetraHydroFuran. The exception to the pairing rule is BV, where the "V" is 2,2-DimethylButane.

Please Note: We are continually improving our knowledge of inks and coatings, to develop better methods and new MSS solutions. UV Process Supply will be glad to help screen for the proper test solution if the standard solvents are not applicable. Chances are that we have a good candidate.

Instructions For Assembling and Running Your Ink-Cure Analyzer:

1. Computer and monitor will connect via cable which is attached to monitor.
2. Ink Cure Analyzer connects with computer via the data cable. There are two connections to be made, multi-pin connector, and biaxial cable with brass colored screw on connector.
3. Level the instrument with the circular level included. A level instrument will prevent the droplet from running during the test. This is important for reproducible results.
4. The needle indicator gauge facing the testing stage reads the air flow over the sample during testing in cubic feet per minute. The air flow is usually preset around 6 CFM. One need seldom change the air flow rate: we recommend that once it is adjusted at 6 CFM no changes be made. Periodically check to make sure flow has not crept up or down but be advised that data generated at some rate of gas flow will not be comparable to data generated at some other rate. Gas flow rate is adjusted with the thumb needle valve found on back of the instrument. A toggle switch found next to the needle valve turns on the air pump. The air pump must always be on during data collection. A small plastic hose located inside the sample arm delivers air flow directly across the sample surface. This air flow is how the evaporation of the droplet is controlled.
5. An evacuation fan runs when testing is not in progress. This small fan can be seen next to the air flow rate gauge. A toggle switch turns on power to the fan. The computer automatically controls fan operation when in the testing mode. When the "Deposit Test Solution" prompt appears the fan will shut off. Exhaust from this fan can either be captured in the activated charcoal filter included with the instrument, or vented by means of a ventilation hose. A hose adapter is included. To insert the hose adapter first remove the threaded filter fixture.
6. Test solution is provided in flame sealed ampules. A handling system is provided consisting of 3 vials with Teflon lined caps, a vapor lock preventer, and a Teflon insertable vial closure. An open ampule of solution will quickly evaporate and must be immediately transferred to a vial.

To transfer test solution to a vial score both ends of the ampule where they begin to narrow. Place the vapor lock preventer on the empty vial. With a lab cloth between thumb and index finger, break one end of the ampule off where it has been scored. Insert the open end in the vial with vapor lock preventer. Invert and allow solution to run into vial. The vial will only partially empty; break off the other end of the vial, again using a cloth to prevent injury. Remove the vapor lock preventer and replace with insertable closure. The insertable closure has a very small opening for insertion of the dispensing needle preventing evaporation of solution.

7. The sample stage is designed with a magnetic hold down ring. A sample about the size of a quarter is required to cover the stage. Place the sample on the stage and anchor with the magnetic ring. There is a provision for vacuum hold down, house vacuum can be applied at the nipple on back of the machine. This option is not often required.
8. To dispense test solution insert the needle into the closure, withdraw the plunger fully. Usually a small bubble will be present. As this bubble is quite small and uniform in size it can be neglected. Dispense the solution with even force in the middle of the sample. Keep the detector head well removed: splashing solution on the detector will cause erroneous counts and confusing data. Dispensing with too much force will spray solution instead of applying an even droplet. Place the head over the sample and push the black start button or the "enter" key.
9. The best area for solution deposition is a solid color or non-printed area. It is quite possible to generate excellent results with printed areas but again, one must take care to deposit test solution on the same spot when comparing one lot to the next.

Your Con-Trol-Cure Ink-Cure Analyzer is constructed for years of reliable service. Besides replacing the Mylar film when contaminated, there is little maintenance. Use the same care you would with any analytical instrument and Your Ink-Cure Analyzer will not disappoint you.

SOFTWARE

1. The software is divided up into three sections: Main Menu, Ink Cure Analysis, and Data analysis. The intent is for the operator to build a data base for future reference. Upon booting up the computer prompts will appear verifying date, time, informing of copyright protection, etc. Finally the main menu will appear. Its options are described on the following page.
2. Background Check: This function verifies that the detector has not been contaminated with test solution. Background levels of 0.5-1.5 are typical for an uncontaminated detector. If counts increase much above this level replace the milar film located on the bottom of the detector.
3. Set Filing Subdirectory: This function offers the option of starting a new filing Subdirectory. Your data will be stored in this Subdirectory. The default Subdirectory designations are as follows: 19940800, which is the encoded date on which the program was set up. Each time a new Subdirectory is started the numeric code is incremented by one. Once a new data Subdirectory is started you can no longer store files in the old one. You can only go forward. You need not use the default designation, up to 8 characters are allowed for file designation. No spaces or punctuation.

4. Set Run Conditions. This function allows the operator to enter all the information concerning the testing about to commence, which will be of interest later when comparing test results. Be sure to verify that the MSS Solution entered is the one you are actually using, that the gas flow correctly entered, etc. There is a space to enter the temperature at which the tests are being run; temperature however does not enter into the data. At UV Process Supply the room temperature is fairly constant and we don't pay much attention to this option. If however tests are being run at press-side where ambient conditions vary drastically it may be useful to have this information stored with your test data.

"Standard Test Comments" are where you can enter the 2 of the 5 comments allowed with each test. This is a good place to enter such information as job or customer identification which will be the same for all tests in a series.

5. Ink Cure Analysis: This should not be the first choice when beginning, The information which will make your data easily understood must first be entered in Section 4, "Set Run Conditions". When Ink Cure Analysis is selected the first prompt will ask for the sample designation. Eight characters are allotted, in keeping with conventional DOS file designation. Avoid periods, slashes and spaces. After pressing "enter" and verifying that your designation is satisfactory you will come to the comment section. If you change your mind about sample designation at this time the only way to go back and make changes is to press "F2" and exit the program.. Notice that you are at comment 3. The first 2 are entered in the standard test comments from "Set Run Conditions". Forgot to enter standard test comments? Press "F2" and restart program.

You may enter up to five comments with each test. Avoid punctuation as this causes problems. When you are done entering comments press "enter" and the " Deposit Test Solution": prompt will appear. Deposit 17 uL of test solution evenly in the center of the sample forming an evenly shaped droplet. Lower the detector head and press the Start Button located on the instrument, or the "Enter" key on the computer. Each test takes 3 minutes.

6. Indices Definitions: This option displays two screens describing the mathematical treatments associated with each MSS Index. These can be printed by pressing the "Shift" "Print Screen" keys at the same time. This part of the program is not interactive.
7. Data Analysis: This is an important part of the program which allows you to compare recent test results to those generated in the past. Selecting option 6 will display the main menu for data analysis which has 5 functions. These are described as follows.

Data Analysis Options

1. "Set Analysis Subdirectory" This function allows the operator to view all the past and present data files and select the one of interest. Note: Changing directory in the Ink Cure Analysis part of the program will not automatically change the data analysis Subdirectory. The most recent one chosen will be displayed as "Present Data Subdirectory. To make a change use the arrow keys on the number keypad, to the right of the standard keyboard keys. Make sure "Num. Lock" (top left of number pad) is off. Once the desired selection is made the main data analysis menu returns.
2. "Analysis of Single Tests": As one would expect data for one test is available in this function. The key feature is that all the information entered in the comments section of "Set Run Conditions" is available. The desired test is selected by moving the number pad cursor and pressing "F8" at the desired test.
3. "Summary Analysis" This function displays the calculated indices for up to 20 tests. Note that data plots are not available in this option. Up to 20 tests can be chosen by moving the number pad cursor and pressing "F8" at the desired tests. To obtain a print out of the data press "Shift" and "Print Screen" at the same time.
4. "Summary Analysis and Plots" This function displays both the calculated indices and the data plots. The first screen will be the indices, press "enter" and the Plots will be shown together on the sample graph. Press "enter" again and an elongated graph which accentuates the differences between tests will be shown. Continue to press "enter" and the program will toggle between these screens. For a print out press "Shift" and "Print Screen" at the same time.
5. "Indices Definitions" This function displays the same screens as in the main menu.

Repairs

There are only two repairs commonly performed by the operator.

Replacement of the Mylar protective film: This becomes necessary when the film is either contaminated with test solution, or torn, which will be evident from high background levels.

(The testing ability of the GM Tube is based on several factors. As the GM Tube emits a signal when gamma rays pass within the vacuum tube, the counting function of this process is infinite. Yet other factors involved in our process relate not this signal, but to the tube maintaining a vacuum. Over time, if the tube begins to fail, it will be due to vacuum failure rather than counting. By repetitive use, the GM tube's organic surface coating can become saturated with C14 (this is why we use Mylar). This saturation can cause the tube to count C-14 exclusive of the test, and can therefore contaminate the test results. If the tube is left to "rest", allowing the C-14 to evaporate, the tube will again be useful.)

Proceed as follows:

A: Remove Allen screw and flat head screw from top of detector head. Note: detector is suspended from set screw, removing this allows the detector to be supported by lift handle (a one inch Allen screw protruding from side of detector head).

B: With lift handle allow detector to descend to the lowest position. Support with one hand while removing lift handle. The detector is now attached only the white air hose and the black electrical wire.

C: The Mylar film is stretched over a stainless steel ring which is held in place by the stainless steel flange on the bottom of the detector head. Remove flange by turning the set screw **IN** (clockwise). Note: Attempting to unscrew this set screw will result in stripped threads. The flange and Mylar ring will slip off . Swing the arm so as to allow the head to hang from the hose and wire attachments. Do Not allow the detector surface to rest on the stage, or touch it with fingers. This mica surface is very fragile. Rupture of the mica will ruin the detector.

D: The Mylar ring will slide out of the flange. Remove the O-Rings which hold the Mylar film to the ring, discard the old film.

E: Place the ring on the Mylar Replacement fixture. Drape a new film over the ring without touching that portion which is to be fastened to the ring. Stretch the O-Rings over ring and seat in grooves on ring side. Gently pull edges of film to remove any wrinkles. Trim Excess.

F: Slide ring into flange and reinstall flange. Flange retaining set screw is to be turned **OUT** (counter clockwise) until flange is retained on detector head. Slide detector up into head and reinstall lift handle. Reinstall head support set screw and flat head screw.

The other repair commonly performed by the user is:

2. **Replacement of entire detector** : Rupture of Mica will necessitate replacement of the entire detector head.

Proceed as follows:

A: Disconnect detector head from its mechanical restraints by following steps A and B.

B: White air hose slides over a nipple on top of detector head. Pry hose up with a spatula or knife. Note: simply pulling the hose will result in its breakage.

C: Disconnect black electrical connection. A male/female snap on connector attaches the detector to lead wire. Detector can now be slid out of head.

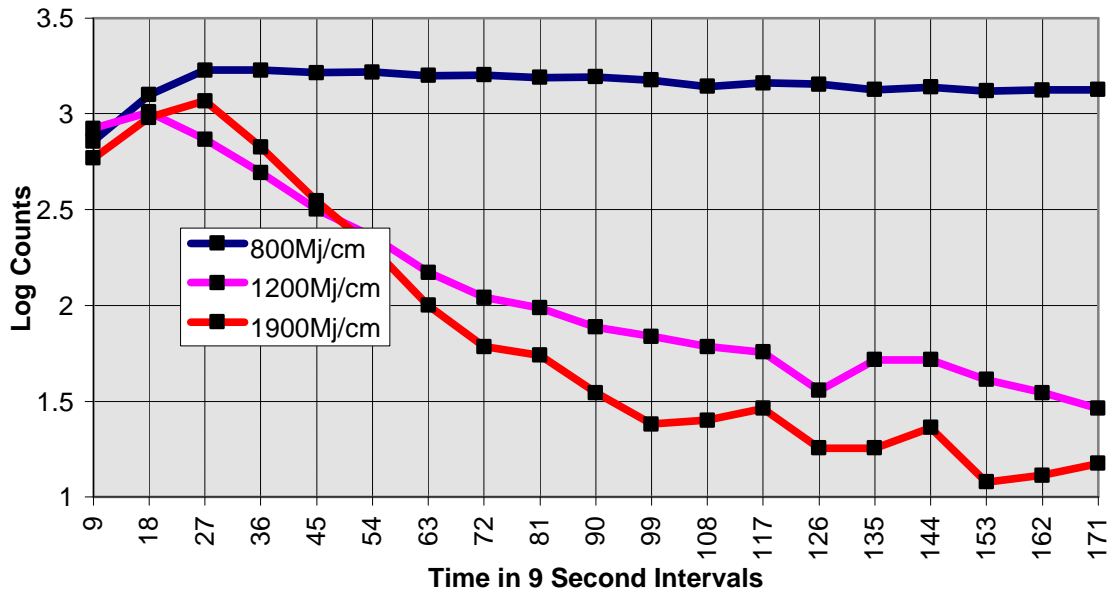
D: Reinstall new detector .

Trouble Shooting Tip:

1: **If a background level reading is 9999:** First check that detector has not been damaged. The mica membrane is visible through Mylar film and need not be disassembled to inspect. Check that all cable attachments are secure. See that circuit board is seated securely.

Data Interpretation:

The following data was generated by running a cure ladder on an epoxy diacrylate coating with a medium pressure mercury vapor lamp. Dosages of 800, 1200 and 1900 Mj/Sq. Cm were applied. Samples were tested with MSS Red. The actual data points were plotted below, and the calculated MSS Indices are shown in the table. Several observations can be made:



- A dosage of 800 Mj is insufficient to affect any crosslinking. A flat curve indicates that complete solvent penetration has occurred and that there is no appreciable crosslinking.
- The index calculations and the Count values are useful in quantifying the results. Higher index numbers are indicative of more thorough cure. Each index is useful in comparing some part of the test to another part. See attached explanation of index calculations.
- All indices increase with higher dosage while Counts decrease. This is indicative of greater crosslinking. As the film becomes more densely crosslinked the MSS solution is unable to penetrate. Notice how dramatic the decrease in counts was between 800 and 1200 Mj/Sq. Cm. There wasn't nearly as much difference between the counts from 1200 Mj/Sq. Cm to 1900 Mj/Sq. Cm.

Sample	Index I	Index II	Index III	Index IV	Counts
800 Mj/Cm	34	49	10	13	28756
1200 Mj/Cm	654	361	339	430	5084
1900 Mj/Cm	1092	631	540	664	4371

What Can We Conclude?

From the three tests we have conducted it is obvious that to cure this coating adequately around 1200 Mj/Sq. Cm is required. Increasing the dosage to 1900 Mj/Sq. Cm is probably not going to be an efficient use of manufacturing capability. Naturally in keeping with good experimental procedure you will probably wish to run more than three tests to draw conclusions.

ICA Data as Quality Control Criteria:

As shown we can characterize the cure response of an ink or coating with an experiment such as the one above. But what next?

This powerful tool is an extremely effective quality assurance device. We have determined at what dosage cure is accomplished. The obvious next step is to set a lower limit for a selected MSS Cure Index to which production must conform. In so doing a reproducible, documentable cure criteria is established. Some of the benefits are as follows:

- Extent of cure can be measured and documented. For ISO 9000 certified manufacturers the task of providing documentation that adequate cure has been accomplished is now convenient.
- The Ink Cure Analyzer stores the QA data in a data base for future retrieval. If there is a question about cure response, conditions, a certain lot of production etc., this data is all retrievable.
- When the cure process is adversely affected by some factor such as failing lamps, dirty reflectors, or other influential factors you are alerted to the trend early.
- Certification of cure can now be provided to your customer.
- Print outs can be attached to job order as certification of cure.

Summary:

1. Run a Cure Ladder
2. Look at all the data including Indices, Counts, and Curve Shape.
3. Establish a minimum value for a selected Cure Index (Index I or III is recommended)
4. In the Comments section of the test enter such identifying information as lot numbers, of the coating used, dosage, and anything else which would be scrutinized if a quality problem related to cure should arise.
5. Take advantage of the database you will generate. Track cure data noting when there is some change in supplier or substrate, etc.
6. When such a change occurs verify that the established criteria is still valid. If not, make an adjustment.

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