

# Direct Measurement of the Rheology of Thin Layers of Reagent During Instant Film Development

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## Abstract

A technique has been developed to measure the change in viscoelasticity of thin layers of reagent during the development of instant photographs. During image development, the developer layer undergoes dehydration, neutralization, diffusion of image dyes, and various other reactions with the negative and the positive receiving sheet, thus changing its rheological behavior.

Using a Paar Physica controlled stress rheometer, a small amplitude strain oscillation is applied to a thin developer layer directly between a negative and a positive sheet, or between one sheet and a stainless steel plate. The instrument measures the storage and loss moduli ( $G'$  and  $G''$ ) and tan delta ( $G''/G'$ ) of the system as a function of time.

This "*in situ*" technique has been used to study the effect of a variety of compositional and process parameters in both the developer and sheet. In addition, it has been useful in modeling system interactions. Good correlation has been shown to both physical and sensitometric final product performance parameters. The technique is being used to monitor the production of developer and sheet, both to predict product performance and to reduce variability. It could also be applied to other systems where a thin layer of fluid interacts with a substrate, resulting in rheological changes to the fluid.

## Introduction

The system studied in this work is the Polacolor peel-apart photosystem<sup>1,2</sup>. This system's three main components are the negative, the positive sheet, and the developer. The negative contains three silver halide emulsion layers, each with an associated dye developer layer in an alkali-permeable polymer. The positive sheet contains a polymeric receiving layer which mordants the dyes. A timing layer is under the mordant layer and controls the diffusion of alkali to a polymeric acid layer. Processing through the camera causes a viscous, alkaline reagent to spread and form a thin layer which laminates the negative to the positive receiving sheet and begins the development process. During development, the dye developers are solubilized in the alkaline

environment. The silver halide is reduced by the dye developers, which become immobilized wherever the emulsion has been exposed to light. The free dye developers diffuse through the reagent layer toward the positive sheet, where they are fixed in the mordant layer and form the positive image. After the designed time period, the timing layer is penetrated by the alkali and the pH decreases as alkali is neutralized and captured in the immobile acid layer. When development is complete, the negative and positive are peeled apart to reveal the finished photographic image.

The thickness and evenness of the developer layer is an important factor in the overall quality of the final photograph. The spreading behavior of the developer is determined by its rheology and both the viscous and elastic properties of the developer are routinely measured and controlled. The physical characteristics of developer change dramatically between initial spreading and peeling. During imbibition, water diffuses from the developer into the sheet and negative, dyes transfer into the developer, the pH drops, and a variety of chemical reactions occur between the negative, developer and sheet. Water uptake alone effectively triples the concentration of polymer in the developer. Clearly the rheology as measured on bulk developer cannot be representative of rheology after processing. The need to quantitatively measure and understand the rheology of developer as it is at the time of peel led to the development of the "*in situ*" technique presented here.

## Experimental

A Paar Physica UM/MC100 controlled stress rheometer with an MP31 50mm or MP32 75mm diameter parallel plate measuring system was used for all rheological measurements, both normal and *in situ*. Although the *in situ* measurements were made in controlled strain mode, it is important that a controlled stress instrument be used. This is because the sheets swell in the presence of the developer to the point that, at the small gap settings used, the plates essentially touch. This could jeopardize the torque transducer in a controlled strain instrument. All pH measurements were made on an Orion Model 720A pH/ISA meter with an Orion ROSS 8135 combination surface pH electrode.

## Description of the “*in situ*” Technique

The “*in situ*” technique measures the rheology of developer “in the situation,” directly between a negative and sheet, and was designed to be a model system for the photographic development process. There are several methods used to monitor the dynamics of the peel-apart laminate. An example is Thymolphthalein testing, which is used to monitor the pH of the positive sheet by observing the color change of an indicator dye. These techniques yield clues to the physical and chemical phenomena occurring during the instant development process. The *in situ* technique presented here examines the instant development process from another viewpoint, that of developer rheology during imbibition.

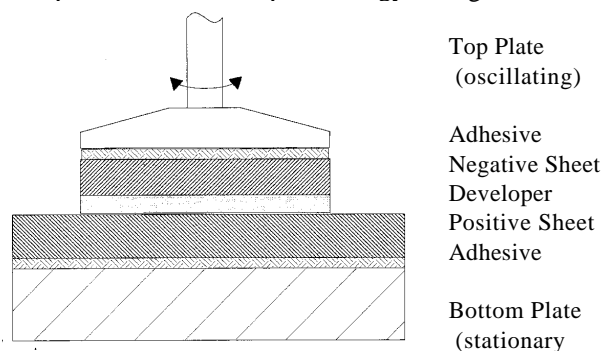


Figure 1: Parallel plates with negative and positive sheet attached for *in situ* rheology.

In order to study the rheology of the thin layer of developer as a function of the changes occurring during imbibition, the parallel plate measuring system of the rheometer was modified, as shown in Figure 1. The plates are sprayed with a light coating of 3M Spraymount Artist's Adhesive and allowed to dry for 2-3 minutes. A mask made from a manila file folder is used to limit the spray pattern to an 80mm diameter circle on the bottom plate, and to protect the instrument from overspray. A piece of negative is firmly pressed onto the upper plate and trimmed to approximate size with scissors. It is then trimmed to the exact size of the plate with a razor blade or sharp knife. A piece of positive sheet is applied to the bottom plate. There is no need to trim the sheet to size. The negative is on top because it has lower mass and because the excess developer on the bottom plate can be more easily scraped from the sheet. The gap is zeroed with the dry negative and sheet adhered to the plates and then the desired gap is set. The gap must be similar to the gap in the actual photosystem in order to have the same stoichiometry. Gaps in the range of 0.02 to 0.15mm have been used. The developer can be placed on either plate, but preferably on the plate bearing the negative sheet. The top plate is then lowered to the preset gap, the edge is cleaned and the test begun. At the end of the test, the top plate is released from the motor and is gently slid off to the side to separate it from the bottom plate. The sheets are peeled from

the plates and discarded. The adhesive may be reused up to ten times before it must be removed with acetone and reapplied.

During the measurement, an oscillating strain is applied to the top plate. Optimum test parameters are dependent on the materials being tested. In general, low frequency (3 to 5 Hz) and low strain (1 to 3 gamma) produced the best results in the systems studied. The phase angle difference between the applied strain and the resulting stress is measured. This stress is separated into its elastic and viscous components. The storage or elastic modulus ( $G'$ ) describes the material's ability to store energy elastically and is the ratio of the elastic stress to strain. The loss or viscous modulus ( $G''$ ) defines the material's ability to dissipate stress through resistance to flow and is the ratio of the viscous stress to strain. The complex modulus ( $G^*$ ) is the vector sum of the two and is the total resistance to deformation. Tan delta is defined as the ratio of the loss to storage moduli ( $G''/G'$ ) and describes the nature of the dissipation of energy for the system. During a measurement, these parameters are recorded as a function of time. Figure 2 shows these curves for a typical system. Since tan delta was found to be most informative, and in order to simplify overlay plots, only the tan delta curves are usually plotted.

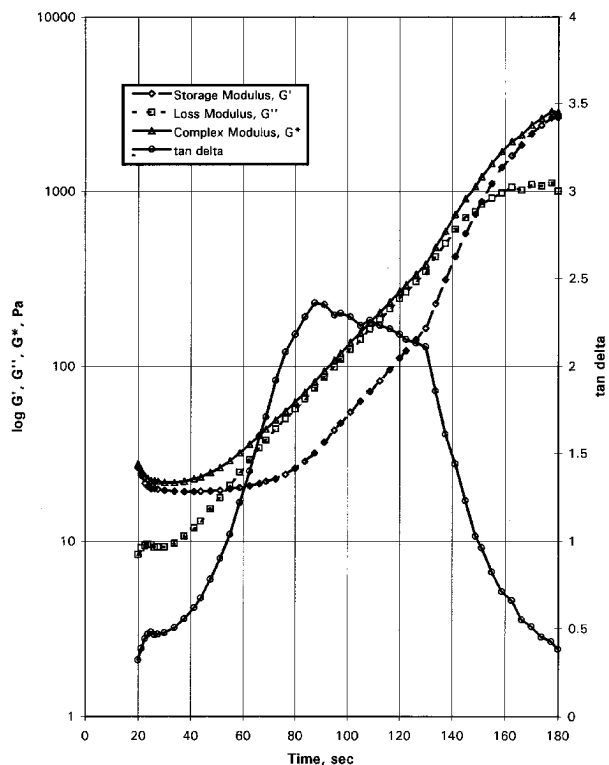


Figure 2: Typical plot of  $G'$ ,  $G''$ ,  $G^*$  and  $\tan \delta$  as a function of time during an *in situ* measurement.

Although having all three components (negative, developer and sheet) present accurately represents the photographic system, it also presents some difficulties. Since the developer-sheet reactions start immediately upon

contact and the developer must be applied to one sheet before the other, there is considerable variability introduced at the beginning of the test. Preparing the top plate is also tedious and time-consuming. This led to the use of a single sheet in the measurement, i.e. either a positive sheet/developer or a negative sheet/developer combination. In this arrangement, adhesive and an untrimmed positive or negative sheet are applied to the bottom plate, the plates are zeroed and the gap is set. Developer is applied to the bare top plate, which is then lowered to the desired gap. In this way, developer does not contact the sheet until the test is started. This procedure results in both operational simplicity and improved precision.

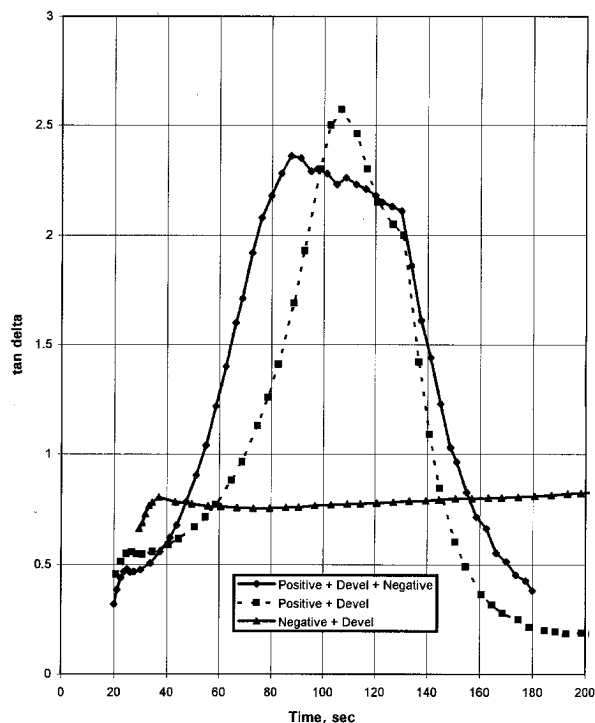


Figure 3: Tan delta curves for: a) negative sheet/developer/positive sheet, b) developer/positive sheet, c) developer/negative sheet.

Figure 3 shows the response of developer with each sheet singly and with both sheets together. Examination of these curves shows that the positive sheet is the major contributor to the rheological changes that occur to the developer during imbibition. The  $\tan \delta$  for the negative sheet/developer is approximately constant and “solidlike” (value less than 1) whereas the  $\tan \delta$  for the positive sheet/developer undergoes a transition from “solidlike” to “liquidlike” then back to “solidlike” behavior. The  $\tan \delta$  for the “full structure” is a modified combination of the two. Developer alone shows no change during the period of the test. Elimination of the negative sheet enhances the ability to characterize the positive sheet/developer interaction. For this reason, all data and graphs presented in this paper were generated from positive sheet/developer testing unless

otherwise specified. For purposes of comparing different components or experiments, several “characteristic values” were established. Two of these are the values at Maximum Tan Delta (MTD) and the time to reach maximum tan delta (TMTD).

### Precision

In order to establish the precision of the technique, repeat tests were run on two different control sheets using two control developers and several production developers. As shown in Table 1, the average TMTD for that series is 105.8 seconds ( $1\sigma = 4.0$  sec) which reflects the intended response time for this system. The variation in the value of MTD reflects the changes in the system response that are caused by the positive sheet (1.9 versus 2.6) and/or the developer (range 2.3 to 3.0). These differences are real and initial work indicates that there is good correlation to dye balance and other sensitometric parameters.

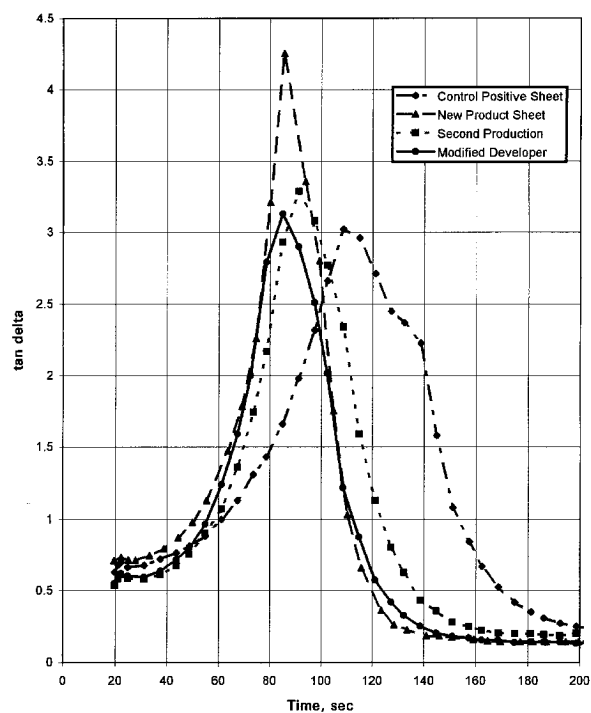


Figure 4: in situ response for a) control positive sheet, b) new product sheet, c) second production of new sheet, d) modified developer with second sheet.

## Photosystem Experiments and Results

### Effect of components

The *in situ* rheology technique was developed to study the effect of individual components and component interactions, as well as manufacturing and processing conditions on overall photosystem performance. The ability of this technique to respond to changes in the photosystem was determined by testing a number of positive sheets and developers known to produce changes in the physical and/or

**Table 1.**  
*in situ* Measurement Reproducibility

System		n	MTD	1 s	Percent	TMTD	1 s	Percent
Positive sheet	Developer							
Control 1	Control A	9	1.93	0.08	4.2	107.2	3.0	2.8
Control 1	Control B	26	1.96	0.17	8.7	105.4	5.4	5.1
Control 2	Control A	19	2.52	0.13	5.2	106.4	4.7	4.4
Control 2	Control B	13	2.67	0.16	5.9	109.5	3.1	2.8
Control 2	G	12	2.71	0.09	3.3	105.0	4.3	4.1
Control 2	R	14	2.39	0.16	6.9	108.8	3.1	2.9
Control 2	S	12	2.69	0.34	12.8	105.6	3.9	3.6
Control 2	T	15	3.01	0.21	6.9	104.1	3.9	3.7
Control 2	V	8	2.69	0.17	6.3	104.0	3.7	3.6
<b>Average</b>		128	n/a			105.8	4.0	3.8

sensitometric performance of the system. Table 2 shows the range of *in situ* response for the tested developers and positive sheets.

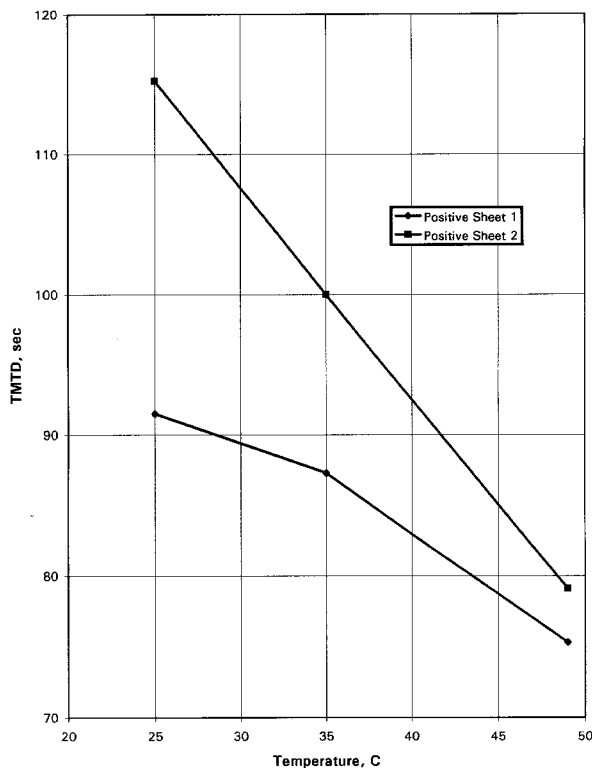


Figure 5: Time to maximum tan delta (TMTD) vs temperature for two positive sheet compositions. A design criterion for a new product was to reduce the normal chemical/physical reaction time by about 20%. Figure 4 shows the *in situ* response for both the new and control positive sheets. The TMTD (time to reach maximum Tan  $\delta$ ) for the control sheet (curve a) is about 106 seconds, while the TMTD for the new product (curve b) is 84 seconds, or

21% reduction from the control value. Thus the rheological performance directionally and quantitatively followed the product design.

An additional quantity of positive sheet was manufactured for this same new product. However, this sheet did not repeat the photographic performance of the first material. *In situ* testing confirmed a difference in the materials (compare Figure 4, curve b to curve c). The TMTD is approximately 7 seconds longer and the curve shapes are different. A developer change was made in an attempt to correct the system response. Figure 4, curve d shows that the response time (TMTD) was reduced by approximately 7 seconds by the modified developer. However, the tan  $\delta$  response of the second sheet and developer are not the same as the original combination. This demonstrates that the system response can be influenced by both the developer and the sheet and has led to an increased understanding of the mechanisms occurring during imbibition.

**Table 2**

Variable	MTD range	TMTD range
Developer	2.1 - 3.7	111 - 153
Positive sheet	1.7 - 4.5	63 - 112

### Effect of Temperature

Although the photographic system is designed to operate within a certain temperature range, the processing temperatures experienced by the customer can vary widely. Understanding the impact of temperature on product performance is critical to the development of systems that are insensitive to this variable. The effect of temperature was tested in the range of 25 to 49 degrees Celsius using two different sheet compositions. Figure 5 shows that the TMTD for one sheet composition is nearly twice as sensitive to temperature change as the other composition. The observed *in situ* response was again reflected in system performance at these temperatures.

### Prediction of Peel Defect

When the negative and positive are peeled apart at the end of development, it is important that the developer layer separate cleanly from the positive and remain with the negative, which is discarded. A product defect results when any of the developer sticks to the positive. This defect is typically only detected after the components are assembled into packs. The tendency of the developer layer to go with the positive sheet or negative during peeling is determined by the balance of a number of forces. These forces include sheet-developer and negative-developer adhesion, developer cohesion, frame assembly factors and conditions, peel speed and angle, etc. One would expect that the response of the developer layer to applied stresses—its rheology—should also influence the peeling behavior of the system.

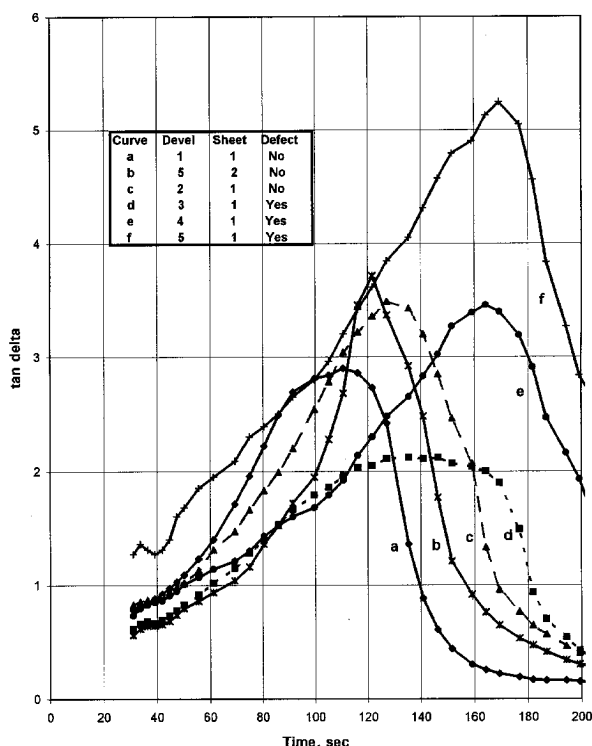


Figure 6: *in situ* response as an indicator of peel defect. Curves a-c do not have the defect while curves d-f represent defective systems

The *in situ* technique was used to study systems known to exhibit this peel defect. The study showed that both the developer and the positive sheet contribute to producing this defect. Ultimately it is the *interaction* of these and other components that creates or prevents the defect. The response of selected combinations of developer and sheet are shown in Figure 6. Correlation of the *in situ* response to peel performance has established that, for this prototype, the peel defect will occur when the tan delta maximum occurs between 155 and 170 seconds. This investigation has enabled the early evaluation of components and the establishment of performance specifications.

The insights provided by this technique have led to a proposal of cohesive failure of the developer layer as a primary mechanism for the peel defect. The defect occurs when the tan delta of the developer is high, resulting in “liquid-like” flow behavior. Surface pH probe work has shown that the pH is about 13 at the maximum point on the *in situ* Tan  $\delta$  curve. Subsequent pH studies in bulk developer confirmed the pH dependent rheological behavior of the developer. pH is an important system design parameter and is influenced by a number of factors. These include the time dependent ability of the positive sheet to hold back and then remove alkali and release water, the ability of the developer to release alkali and absorb water, and finally the specified “peel time” of the system. Subtle manufacturing variations in the developer and especially in the positive sheet can influence this time dependent pH and subsequent rheological behavior. The *in situ* technique provides a tool for identifying and controlling the sources of this variability.

### Conclusions

A technique has been developed to measure the rheology of developer directly in contact with negative and positive sheet. The response of this measurement correlates well with other physical and photographic behaviors of the system. The *in situ* technique provides a quantitative parameter that can be used to: 1. monitor individual components during production, enabling the identification and control of sources of variability; 2. reduce the time and resources needed to diagnose and solve problems; 3. develop a better understanding of system interactions and mechanisms; 4. design new products with improved system performance. The technique could also be applied to other systems where a thin layer of fluid interacts with a substrate, resulting in rheological changes to the fluid or to situations where direct contact between the material and the plates is not desirable, such as measuring the setup of resins or adhesives.

### Acknowledgments

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