This is to certify that the

thesis entitled

Feasibility Study on the Application of a
Film Based Thermal Sensor

presented by

John Gerald Betts

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chem. Eng.

Major professor

Date 8/6/93

O-7639

FEASIBILITY STUDY ON THE APPLICATION OF A FILM-BASED THERMAL SENSOR

By

John Gerald Betts

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1993

ABSTRACT

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By

John Gerald Betts

Many industries depend on products that require specific temperature control and storage. With this dependence in view, an alternative to electronic thermal monitoring has been proposed utilizing a film-based chemical sensor. A titanium based film on a glass substrate will react with a catechol-like compound giving a colorimetric measurement. This color change can be used qualitatively and quantitatively to determine the time-temperature history of products. Use of this sensor appears feasible in the temperature range of 65 to 140°C for time-temperature monitoring; however, use in the -20 to 30°C temperature range only appears feasible for the determination of the maximum temperature achieved. An indicator for temperatures between 30 and 65°C may also be feasible, based on the performance of the high temperature sensor.

This work is dedicated to my parents, my sister, and especially to
Julie without whose support this work would not have
been possible.

ACKNOWLEDGEMENTS

I would like to express my deep sense of gratitude to my advisor, Professor Kris Berglund, for his encouragement and guidance throughout the course of this work.

I would also like to thank Drs. Beatrice Torgerson and Joel Dulebohn for their assistance and background work used for this project.

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1. INTRODUCTION

1.1 Scope

Many processes depend on raw materials that must be stored at specific temperatures. Composite prepregs, frozen food storage, and thermal food preparation are all examples of fields that rely on keeping materials at specific temperatures. Quality control and safety assurance of these products may be determined by the thermal history profile. Several types of technologies exist for measuring the time-temperature profile of substances. These processes are expensive, complicated, or lack quantitative information on the time-temperature history. The development of an inexpensive, reliable, qualitative and quantitative time-temperature sensor would allow more effective and controlled use of materials that are stored or processed under strict thermal conditions.

1.2 Preview

The initial thrust of this project was the determination and construction of a cold time-temperature sensor. We intended to produce a film-based colorimetric indicator that could be used qualitatively and quantitatively to determine the time-temperature history of a storage or processing environment. Indicator chemicals were to be dissolved in solvents that had melting points ranging from -20°C to 19°C. These indicator solutions would then be frozen to the film covered substrate. The completed unit of substrate, film, and indicator solution would comprise a time-temperature sensor specific for the melting point of that solvent. The use of multiple sensors with solvents of different melting points was desired to give a detailed time-temperature history profile. As the individual solvents reach their melting point temperature, the indicator chemical will begin reacting with the film causing the film to turn color. A schematic of this sensor is shown in Figure 1 (on the following page). Absorbance studies of the color change intensity and kinetic reaction data could be used to calculate the

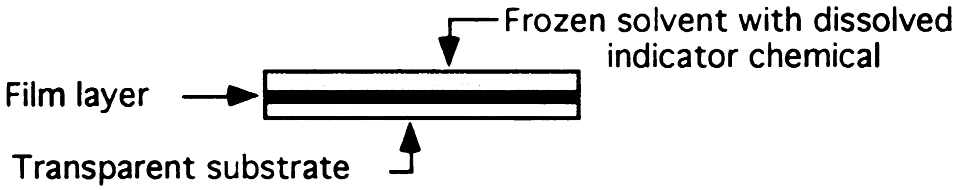


Figure 1 Sensor schematic.

thermal history of the sensor. The requirements for this low-temperature sensor would include: quantitative and qualitative color change of the film and quenched reaction below solvent melting point.

Synthesis of the film, determination of a suitable indicator chemical, and solvent studies were required and performed to determine a suitable low-temperature sensor. Problems developed with these cold temperature sensors, including poor quenching of the color change reaction after returning to temperatures below the solvent's melting point. Therefore, subsequent studies were focused on a high temperature sensor with the hope that these problems could be minimized. High temperature sensors have also received less attention than the cold temperature sensors as indicated by the availability of commercial products(Taoukis[1]). The second alternative use of this approach, an elevated temperature sensor, if practical, would also greatly benefit many industries, especially the food processing companies.

Currently, monitoring of sterilization is done manually by quality control personnel, and very little information on the temporal component is obtained. The advantage of the proposed high temperature sensor would be to record and store the time-temperature exposure profile of a process by means of a colored chemical reaction. The optical reading from the sensor can then be integrated and related to calibration curves to validate the process. Additionally, since this proposed sensor would be used for on-line validation of thermal processing, the color change reaction would not have to be completely quenched. Quenching of the reaction would not be important since measurements are made immediately following processing. This contrasts with the cold-temperature sensor since for storage processes at low temperatures the sensor may not be measured until days after the storage temperature exceeded the melting points of the solvents.

The high temperature sensor is identical in design to the cold temperature sensor, with the exception of different solvents with melting points ranging from approximately 65°C to 120°C. In this work, determination of the appropriate indicator chemicals, solvents, and films were accomplished for this temperature regime. Kinetic studies over the temperature range of 65°C to 140°C were performed. The resulting data was analyzed using a kinetic model which is based on a first order rate law describing consumption of the reactive sites in the film in an attempt to construct suitable calibration curves. Results of the analysis indicate that the sensor does appear to generally follow a first order type kinetic rate expression. These results indicate that the high-temperature film-based sensor may be a feasible method for determining the time-temperature profile of materials. Ultimately, useful calibration curves need to be established before the proposed device can be used as a commercial sensor.

2. LITERATURE SURVEY

2.1 Current Sensors

The determination of the time-temperature history of materials is an area that has used a variety of technologies in the creation of sensors. Enzymatic, acid-base, diffusion, electronic, and combinations of these types can all be used to determine the time-temperature history of a substance. The sensors that have been examined deal almost exclusively with low temperature (frozen food storage) conditions. A good introductory reference about these low temperature sensors is a paper by Taoukis[1]. Examination of the sensors based on these different techniques will illustrate one or more drawbacks in the determination of the time-temperature profiles of the environment.

Enzymatic indicators have been patented by Blixt[2] and Agerhem[3], among others. This type of sensor uses a color change indicator based on the change in pH caused by a controlled enzymatic reaction. The enzyme is physically separated from the substrate and indicator by means of a breakable barrier. Once this barrier is broken, the enzyme and substrate/indicator are allowed to mix, and the reaction is started. The indicator's pH measurement can give the time-temperature profile of the sensor if the enzyme activity is included. As temperature increases, enzyme activity increases, and the pH will change at an accelerated rate. Drawbacks of this sensor technology include denaturing of the enzyme at extreme temperatures and the requirement of physical destruction of the separation barrier.

Shafer[4] and Jalinski[5] have both patented an acid-base thermal exposure indicator used to determine the expiration of shelf-life of materials. This device uses a chemical that reacts at a rate depending on time, temperature, and pH to produce an amine. An indicator chemical is also incorporated into the sensor which reacts independently, depending on time, concentration, and pH. Once one of these chemicals is consumed, an acid-base reaction occurs, and the rapid change in pH causes a color change. This indicates the completion of the two independent reactions. Variations of the concentrations of these chemicals can be used to create a sensor for materials with a specific shelf-life at a specified temperature. The ambient temperature controls the reaction rate. The concentrations of the reactants control the length of time until the end-point of the reaction is reached. Since this indicator uses an end-point, no information on the time-temperature history of the sample can be obtained.

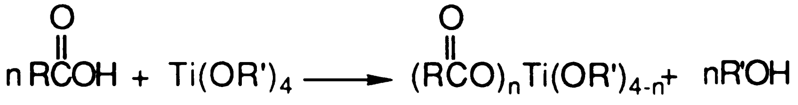
Several types of diffusion-based sensors have been studied and patented. Manske[6], Patel[7,8,9], Allmendinger[10], and Arens[11], among others, have all patented a diffusion-based, time-temperature device. Manske uses a fluid pad attached to a wick containing an indicator to measure the progress of the fluid. Patel has indicators that use both liquid and vapor diffusion through a medium to measure time-temperature profiles. The reactant moves through a porous medium reacting with an indicator, giving rise to a visible moving boundary. Allmendinger has produced a device suitable for six month storage times of frozen foods, using a diffusion based system. Arens utilizes a rubbery polymer that diffuses and renders transparent the diffusion barrier. These indicators all have one or more of the following drawbacks; relatively complicated design, endpoint indication or lack of time-temperature profiles, and physical activation by removing a barrier required.

Electronic time-temperature indicators range from computer monitoring using thermocouples, to Kang's[12] process of electrochromatic reactions. Computers can be interfaced to thermocouples and used to monitor the time-temperature profile of materials. Karr[13] uses a small integrated circuit and galvanic consumable electrode as a coulometric indicator. This charge transfer is the electronic equivalent of change in reaction rate as a function of temperature. Lastly, Kang[12] uses an electrochromic diffusion material that changes color as electrons diffuse from the electron source to the electron sink. These methods are all relatively complex, and assumed to be expensive to manufacture.

2.2 Films

The films required in this study must be optically clear, resistant to solvents, reactive with the indicator, and able to give a homogeneous coating on a substrate. Sol-gel chemistry is a field that can produce materials in different forms: solutions, films, and gels. Titanium is a metal that may form metal-ligand bonds with a possible corresponding color change. Combining these two factors, Anderson[14] and Dunuwila[15] discuss the formation of a membrane or film coating made from inorganic titanium oligimers with attached organics using controlled hydrolysis of titanium alkoxides in water and acids. The generalized sol-gel process, as illustrated in Figure 2 (on the following page), is reproduced from Anderson[14]. The abundance of possible routes in the sol-gel process indicates that specific procedures must be followed to yield the product of choice.

Three types of reactions may occur in the preparation of sol-gel inorganic films: acid reactions, hydrolysis, and condensation (Kirk-Othmer[16]). The ratios of acid and water to the titanium alkoxide determine the formation of the final product, be it a gel, solution, or colloid. The reaction of titanium alkoxides with carboxylic acids is illustrated in Figure 3. The acid reaction allows the replacement of one or more of the OR functional groups attached



$$n\,R\overset{\overset{O}{\|}}{C}OH + Ti(OR')_4 \longrightarrow (R\overset{\overset{O}{\|}}{C}O)_nTi(OR')_{4-n} + nR'OH$$

Figure 3 Titanium alkoxide/carboxylic acid reaction.

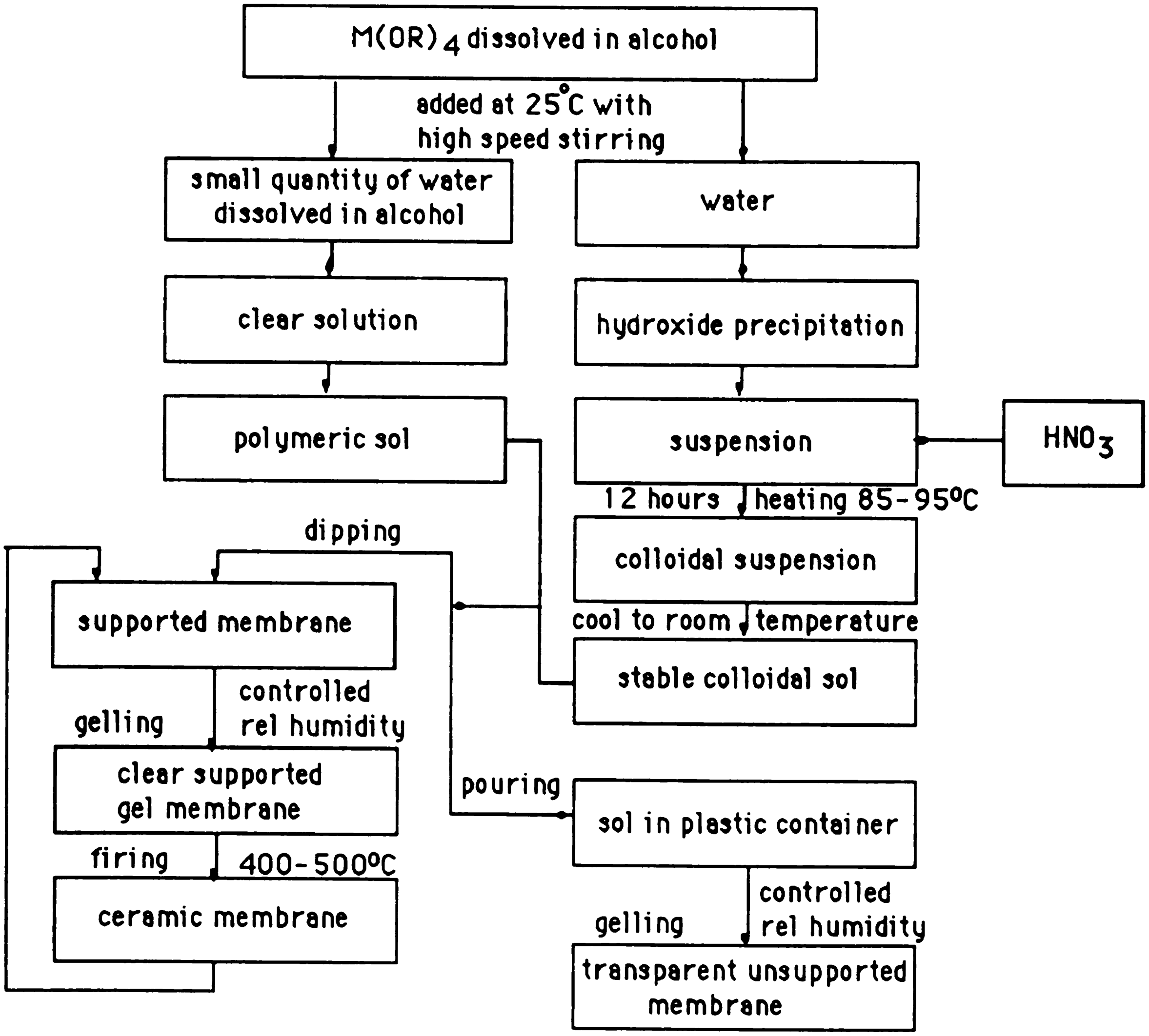
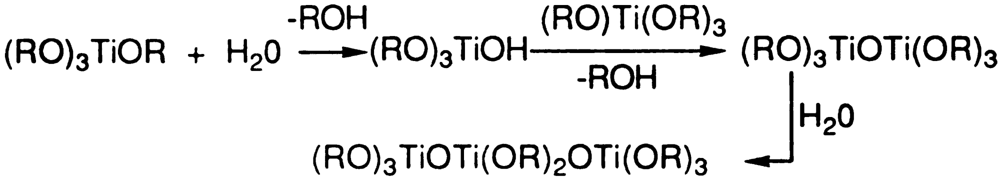


Figure 2 Sol-gel products flowchart.

to the titanium with the corresponding carboxylic acid groups. This acid reaction may affect the kinetics and yield of the condensation and hydrolysis reactions by steric hindrance. The hydrolysis and condensation reactions cause the titanium alkoxide to polymerize into linear, and possibly branched structures. The generic hydrolysis and condensation reactions are shown in Figure 4. The condensation reactions occur in the last two steps of this equation. The combination of these two reactions allows the formation of a organometallic backbone with attached organic groups that is suitable for film coatings. Yoldas[17] states that:



$$(RO)_3TiOR + H_2O \xrightarrow{-ROH} (RO)_3TiOH \xrightarrow[-ROH]{(RO)Ti(OR)_3} (RO)_3TiOTi(OR)_3 \xrightarrow{H_2O} (RO)_3TiOTi(OR)_2OTi(OR)_3$$

Figure 4 Hydrolysis and condensation reaction of titanium alkoxide.

> "This is done first by controlling the amount of water and dilution of the system, and second, by the presence of a critical amount of certain acids...solutions are useful in depositing optical titania coatings..."

Therefore, the reactions represented in Figure 3 and 4, when used with the appropriate amounts of water and organic acids, should allow the synthesis of a solution that can be used to coat a substrate with an optically transparent film.

2.3 Indicator Chemicals

Use of a film that incorporates a metal ion suggests that a metal-ligand reaction may occur. Textbooks, including Masterton[18], indicate that metal-ligand species generally show intense colors. Ligands are, in principal, any molecule or anion with an unshared pair of electrons, such as, NH_3, H_2O, OH^-, and Cl^-. Kirk-Othmer[16] states in Encyclopedia of Chemical Technology that:

> "Phenols react readily with TPT(tetraisopropoxytitanium) and the equilibrium lies far to the right, especially with diphenols, such as substituted catechol and...products are yellow or orange."

This suggests that a bidentate ligand, such as catechol or pyrogallol, may react with the titanium-based film giving rise to a color change. These bidentate ligands have hydroxyl functional groups that reacts with the titanium similar to the diphenols discussed by Kirk-Othmer[16]. The mechanism of this titanium to indicator reaction and color change is not well understood since the composition and structure of the film has not been determined. Cotton[19] and Pierpont[20] discuss the possible binding of catecholates to metal complexes. These authors believe that both OH groups of the catecholate bind or complex to the metal atom in the organometallic complex. Determination of possible indicator chemicals is now a matter of searching through various catalogs and references including: Aldrich[21], Sigma[22], and the Merck Index[23]. These possible indicator chemicals should have two functional groups consisting of unshaired electrons, should be non-toxic and stable, and should be inexpensive.

2.4 Solvents

Solvents required for this project must dissolve the indicator chemical in sufficient amounts to allow reactions to occur with the film. These same solvents should not degrade or react with the film. The solvents should also be non-toxic and have a low vapor pressure with specific melting points appropriate to the desired temperature range. The melting point of the solvent will determine the temperature at which the reaction between the indicator and the film will begin. Catalogs and references such as Aldrich[21], Sigma[22], and the Merck Index[23], can be used to select possible solvents on the basis of melting point and reactivities. Trial and error experimentation with the indicator and film would most likely be the only method of determining if these solvents are acceptable for a time-temperature sensor.

3. MATERIALS

3.1 Films

Our research group has been primarily concerned with the use of two different substrate films. The two films are based on titanium tetra-isopropoxide, water, and either valeric or valeric and lauric acids combined. The films produced are optically clear, scratch resistant, and stable. The films can be easily spin-cast onto a glass or other type of substrate by the use of a tabletop centrifuge.

During the course of this study, preparation methods for the films were changed as a result of new information supplied by Beatrice Torgerson during internal lab discussions. This new method of film preparation was introduced at the same time that our emphasis switched from the cold temperature to the high temperature indicator studies when it became apparent that the low temperature sensor could not be quenched. The low temperature (-20°C to 30°C), original film preparation materials and concentrations are illustrated in Table 1 on the next page. The two major film types are based on valeric or lauric/valeric acids combined with titanium tetra-isopropoxide and water. All chemicals were supplied by Aldrich and used without further purification. The water is deionized by reverse osmosis(RO) to 18 MΩ x cm resistivity. The film components are combined in the top-down order given by the table with sufficient mixing by vortex stirrer to ensure a homogeneous solution. Mixing of the solution should occur between all additions of chemicals. The final solution can then be applied to the substrate.

Table 1 Original film composition.

	Valeric Acid Based		Lauric/Valeric Acid Based	
Species	Amount	Ratio	Amount	Ratio
Valeric Acid	1.65 ml	9.03	2.50 ml	6.84
Lauric Acid	0.0 g	0	250 mg	0.37
Titanium Isopropoxide	0.5 ml	NA	1.0 ml	NA
RO Water	46 µl	1.52	46 µl	1.52

The ratios are included in Table 1 since the sol-gel field of chemistry routinely uses this type of nomenclature. All ratios are compared to titanium tetra-isopropoxide on a molar basis. The acid ratios to titanium are normally given the symbol R_a while the water ratio with respect to titanium is given the symbol R_w.

The incorporation of the lauric/valeric based films resulted from experiments performed by Beatrice Torgerson. It was discovered that stearic acid, a possible indicator solvent (see section 3.3), caused the valeric acid based film to dissolve. Therefore, the lauric/valeric based film was included as a possible alternative that may resist degradation in a stearic acid solvent environment.

High temperature (greater than 60°C) studies incorporated the new film preparation techniques determined by Torgerson, Dunuwila, and Berglund[24]. They determined that the Raman spectra for the film solutions did not change appreciably when the R_a was between six and nine. Joel Dulebohn had also performed experiments with these film preparations with good results as discussed in available internal lab notes. Since this new film preparation produced stable and homogeneous films and had been used successfully before, this method was adopted. The preparation and concentrations of the new films are shown in Table 2. The preparation of the lauric/valeric acid based film begins with the mixture of both acids. Once the lauric acid has dissolved in the valeric acid, titanium tetra-isopropoxide is added and stirred on a vortex mixer. This solution is allowed to react for at least 6 hours in the dark. Lastly, the RO water is added and again agitated on the vortex mixer. This final solution is placed in dark storage for at least 12 hours before being applied to the glass substrate. The valeric based film is prepared identically without the addition of the lauric acid.

Table 2 Current film composition.

	Valeric Acid Based		Lauric/Valeric Acid Based	
Species	Amount	Ratio	Amount	Ratio
Valeric Acid	2.7 ml	7.39	2.55 ml	6.98
Lauric Acid	0.0 g	0	250 mg	0.37
Titanium Isopropoxide	1.0 ml	NA	1.0 ml	NA
RO Water	88 µl	1.46	88 µl	1.46

Zirconium based films were also prepared to determine if a non-reacting zirconium film layer would affect the time-temperature color change reaction. The composition of the zirconium based solution is given in Table 3.

Table 3 Zirconium film composition.

Species	Amount	Ratio
Valeric Acid	1.7 ml	7.0
Lauric Acid	250 mg	0.55
Zirconium n-Propoxide	1 ml (70 wt.%)	NA
RO Water	60 ul	1.49

The zirconium propoxide was obtained from Aldrich and used without further purification. This zirconium film solution was prepared using the same techniques as the lauric/valeric film new preparation discussed above.

All film solutions can be applied to a glass substrate using a sample spinning method. A disposable glass Pasteur pipette (VWR cat. no. 14673-043) was used to spread the required amount of solution onto the substrate. Enough solution should be applied so that during sample spinning, the solution should be spread uniformly over the substrate. Sample spinning should occur for at least 5 minutes. A shorter spinning time, 1 minute, can be used if the film/substrate is then allowed to dry overnight in a dark, clean environment. The zirconium based solution can be applied over previous film layers by the same method. Our studies used an International Clinical Centrifuge with the glass substrate centered and affixed to the hub of the rotor with double sided tape and oriented horizontally. The substrate used was pre-cleaned microscope slides from Erie Scientific (No. 2954-F) cut into strips insertable into the spectrophotometer cuvette. These slides were approximately 1x2.5 cm in size and required approximately 2 drops of solution. Spinning of these precursor solutions result in a uniform film layer of approximately 3000Å in thickness. This film thickness was determined using profilometry studies on the films performed by Joel Dulebohn during the course of his research and discussed in internal lab notes.

Films can also be calcined by heating in an oven set at 400°C or more for approximately 8 hours. This heating appears to convert the film into a ceramic membrane as shown by the flowchart in Figure 2 contained in section 2.2. Preliminary tests of calcined films indicate that no reactions occur with indicator chemicals.

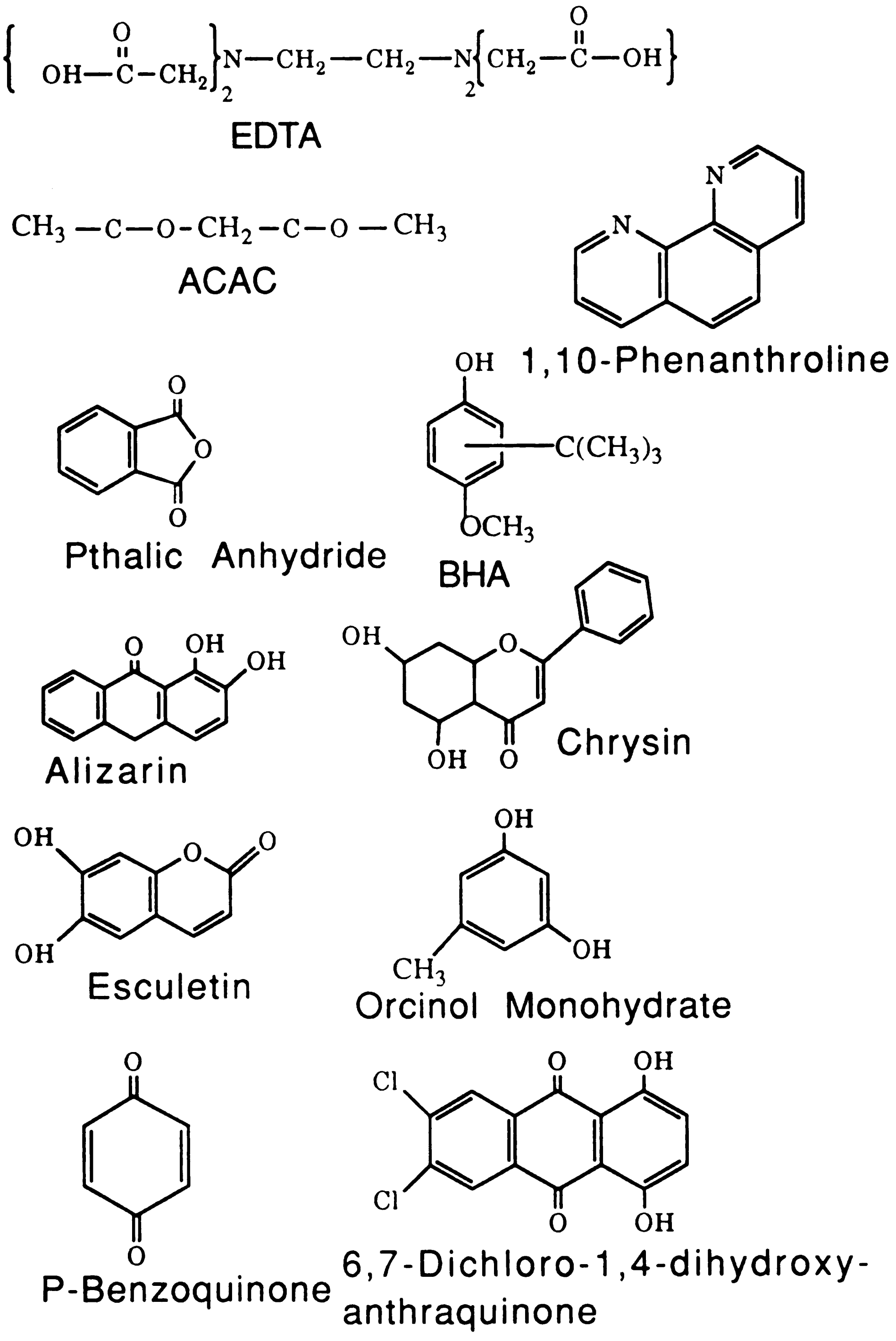
3.2 Indicator Chemicals

3.2.1 *Low Temperature*

Kirk and Othmer[16] state that "Phenols react rapidly with TPT(tetraisopropoxytitanium)...products are yellow or orange." Phenols are hydroxy substituted benzene rings. Barrow[25] discusses that colored compounds often involve aromatic rings. Combining these two statements indicate that possible indicator chemicals would consist of an aromatic ring with attached hydroxy groups. Cotton and Wilkinson[19] state that catecholates are known to react with metals in solution. These known solution reactions with this type of chemicals will hopefully work similarly in the solid film system that we are trying to develop.

The actual mechanism of the indicator to metal reaction is unknown since the film has not been completely characterized to this date. As discussed in section 2.3, it is believed that both OH groups bind to the metal. It is unknown whether the indicator OH group displaces a titanium-organic bond or if the indicator OH group changes the coordination number of the titanium. Since we believe that the film is stable in normal conditions and solvents, this would lead us to believe that the indicator changes the coordination number of the metal, although, this has not been proven. Since the film shows no signs of degradation after the addition of the indicator, we believe that the titanium coordination is changed from four to six with the addition of a catecholate indicator.

Chemicals containing an OH functionality tested for the low temperature sensor include: pyrocatechol, pyrogallol, phenol, P-chlorophenol, 1-napthol, P-nitrophenol, anisole, benzoic acid, sodium benzoate, P-benzoquinone, 2,4-dichlorophenol, tetrachlorocatechol, pentachlorophenol, and alizarin. The chemical structure of these molecules, among others, is included in Figure 5 on the following pages.



EDTA

ACAC

1,10-Phenanthroline

Pthalic Anhydride

BHA

Alizarin

Chrysin

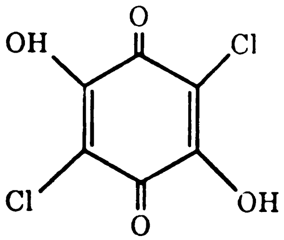
Esculetin

Orcinol Monohydrate

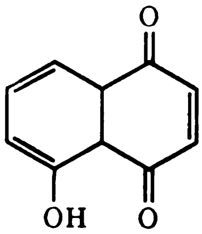
P-Benzoquinone

6,7-Dichloro-1,4-dihydroxy-anthraquinone

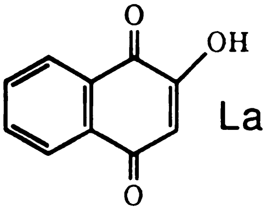
Figure 5 Chemical structure of indicators.



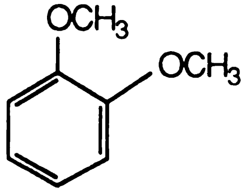
2,5-Dichloro-3,6-dihydroxy -p- benzoquinone



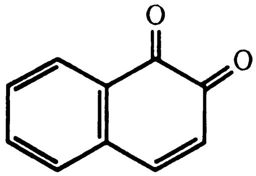
Juglone



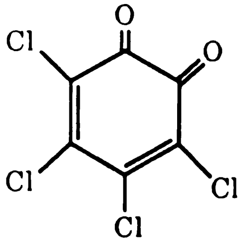
Lawsone



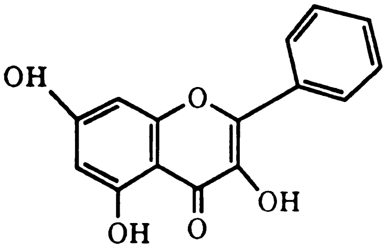
Veratrole



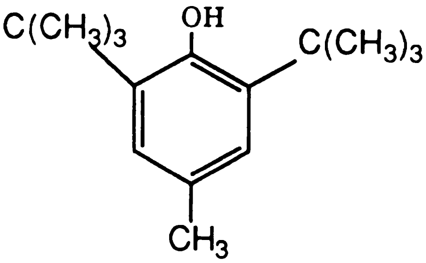
1,2-Naphthoquinone



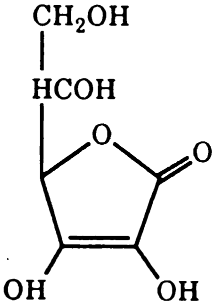
Tetrachloro-1,2-benzoquinone



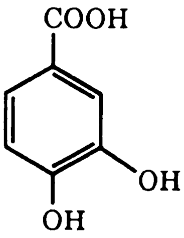
Galangin



BHT

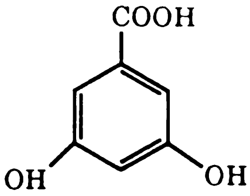


Ascorbic Acid

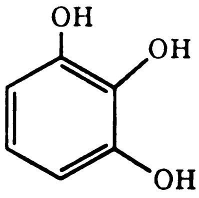


3,4 Dihydroxy Benzoic Acid

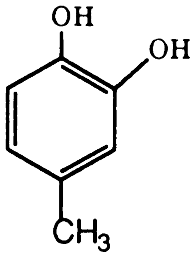
Figure 5 (cont'd)



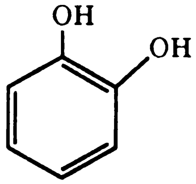
3,5 Dihydroxy Benzoic Acid



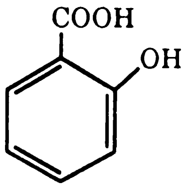
Pyrogallol



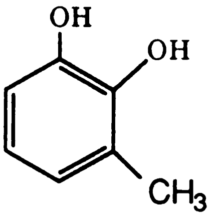
4-Methyl Catechol



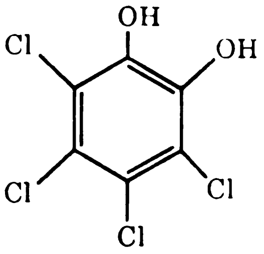
Catechol



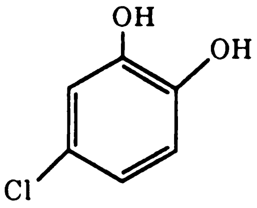
Salicylic Acid



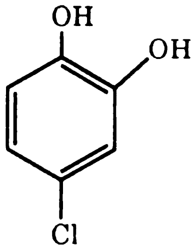
3-Methyl Catechol



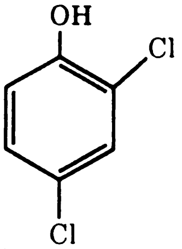
Tetrachlorocatechol



5-Chlorocatechol

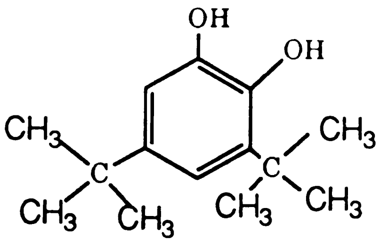


4-Cholrocatechol

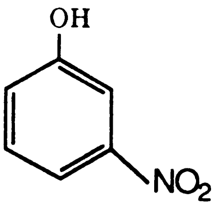


2,4-Dichlorocatechol

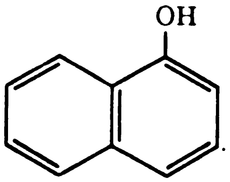
Figure 5 (cont'd)



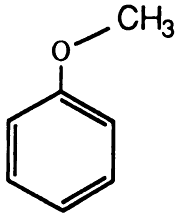
3,5-Di-t-butylcatechol



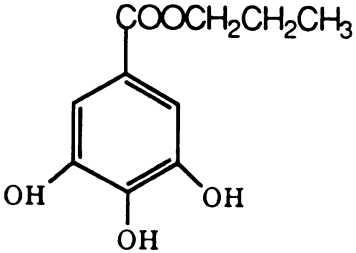
P-Nitrophenol



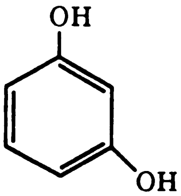
1-Napthol



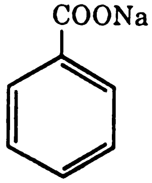
Anisole



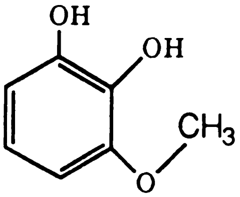
N-Propyl Gallate



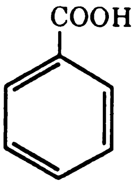
Resorcinol



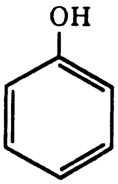
Sodium Benzoate



3-Methoxycatechol



Benzoic Acid



Phenol

Figure 5 (cont'd)

3.2.2 *Elevated Temperature*

The possible indicators that were selected for trials for the high temperature region were chosen from the chemicals available in our lab that had a OH functional group. Catechol type chemicals with a hydroxy functionality were selected for testing as discussed in section 2.3 and 3.2.1. Chelating chemicals were also tried since these agents (EDTA, acac, and others) often produce colored reactions with metals. Natural products (BHA, BHT, and flavones) that would be acceptable to the food industry were an additional group that was qualitatively studied. The structure of all these possible indicators, among the low temperature indicators, tested is shown in Figure 5 found in the previous section. Again, as discussed in section 3.2.1, any indicator chemical should react with the titanium incorporated in the film and give a visible color change within a reasonable amount of time without degradation of the film.

3.3 Solvents

The choice of solvents for the indicator chemical is determined by the temperature threshold required for the sensor. At the melting point of the solvent, the dissolved chemical and cast film will begin to react giving rise to a color change. A partial list of possible solvents is given in Table 4 on the following page. It was discovered that stearic acid dissolved the valeric based films as discussed in section 3.1. We also determined that the lauric/valeric based film would degrade in stearic acid. This degradation of the films suggested a shift in emphasis from the acids to the use of waxes as solvents for the indicator chemicals in the high temperature regime. Commercial candle paraffin wax (Gulf@ wax) with a melting range of 51°C to 53°C was successfully utilized. Moreover, in order to meet a variety of temperature thresholds for the sensor, wax blends were graciously provided by IRM (Industrial Raw Materials). Namely, IRM #8618 and Hewax with melting points of 80-84°C and 110-118°C respectively, were investigated. Other solvents may be acceptable if they are transparent to the wavelengths of light detected, dissolve sufficient

Table 4 Solvents and their melting points.

Solvent	Melting Point, °C
Diethyl Succinate	-20
Diethyl Maleate	-10
Diethyl Fumarate	1-2
Monoethyl Succinate	8
Dimethyl Succinate	19
Lauric Acid	44-46
Paraffin Wax	51-53
Stearic Acid	67-69
IRM #8618 Wax	80-84
L Malic Acid	101-103
IRM Hewax	110-118
DL Malic Acid	131-133

quantities of indicator chemicals, and do not react with the film or substrate. The solvents we primarily used during the course of this study were diethyl fumarate, dimethyl succinate for the low temperature studies, and the 3 waxes listed in Table 4 for the work at elevated temperatures. The melting points of these solvents were determined from the Merck Index[21] and through Industrial Raw Materials(IRM) Corporation representatives for the wax blends.

It is important to mention that for a practical application, it might be necessary to use multiple sensor strips with different solvents in order to obtain more precise information on the time-temperature history of the environment. As the lowest melting point temperature is reached, an imbedded film sensor will begin to react. When the next lowest temperature is obtained, the second film sensor will proceed with the color change reaction. The time between the lowest and next lowest melting point temperature will be indicated by the increased intensity of the color of the first film compared to the second film and taking into account the change in reaction rates as a function of temperature.

4. RESULTS

4.1 Low Temperature Sensor

4.1.1 *Construction and Materials*

The construction of a cold temperature (-20°C to 30°C) sensor involved first determining the appropriate materials. The valeric acid based film (original preparation) was chosen for ease of synthesis. Diethyl fumarate was also chosen as the solvent since the melting point is approximately 0°C which would be important in the frozen food storage industry.

The indicator chemical for the cold temperature sensor was chosen from the chemicals discussed in section 3.2.1 and illustrated in Figure 5. Low concentrations of possible indicator chemicals were dissolved in diethyl fumarate and allowed to react with the valeric acid based film coated glass slide for long periods of time. Visual inspection for a color change of these films over time indicated if the chemical was an acceptable indicator. Other phenomena that would affect the sensor performance, such as solution color changes or film degradation, were also noted. In all cases, the reaction was studied at 32°C. The compounds that were most effective in producing a color change in the film were pyrocatechol, commonly known as catechol, and pyrogallol. P-nitrophenol and 1-napthol also gave reasonable color changes. The intense color changes and long reaction times that occur with such low concentrations indicate that these chemicals may be very efficient indicators in the low temperature region.

Further optimization of the low temperature indicator chemical was performed with catechol and pyrogallol. A kinetic curve was constructed from reactions of these two chemicals in diethyl fumarate at 32°C. This curve is shown in Figure 6.

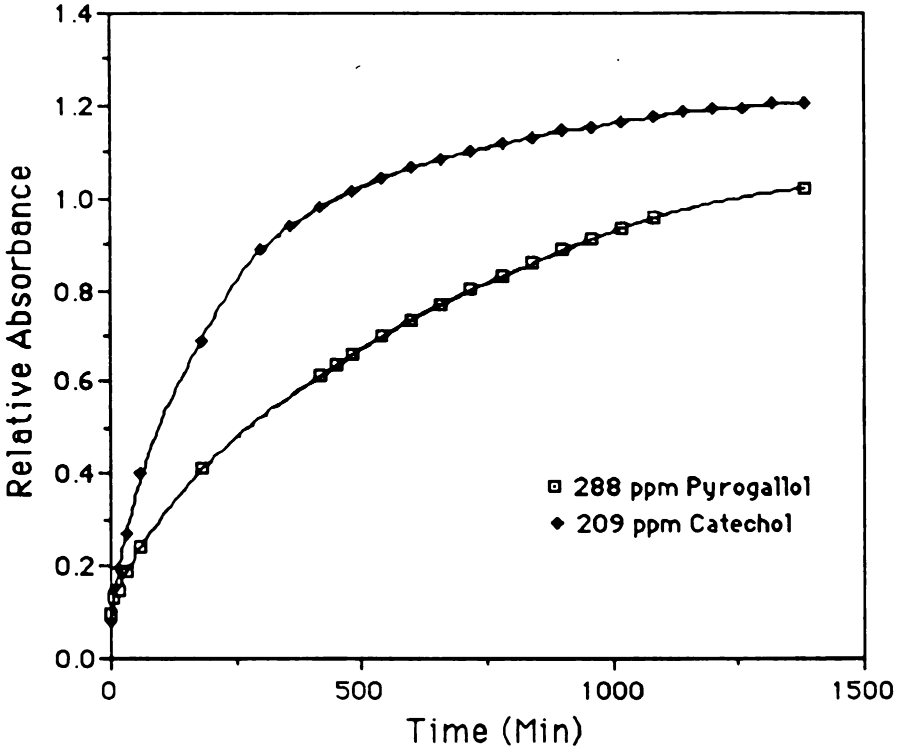


Figure 6 Absorbance as a function of time for pyrogallol and catechol in diethyl fumarate reacted with titanium based film at 32°C.

The relative absorbance reading was determined by the difference in intensities between the baseline, 700 nm, and a location on the peak maximum that corresponded to 440 nm for catechol and 450 nm for pyrogallol. Of these two indicators, catechol was chosen as the optimal low temperature indicator since catechol gave a more intense absorbance reading.

Various methods were attempted at forming a self-contained sensor. One method attempted was to spray a fine mist of catechol-containing dimethyl succinate to a glass slide that had been cooled to approximately -195°C by immersion in liquid nitrogen. This method displayed an intense color change after storage for 4 days in a freezer at -18°C. Mist spraying of pure dimethyl succinate onto a liquid nitrogen cooled slide followed by a mist spraying of catechol in dimethyl succinate also displayed a color change after 4 days storage in a freezer. This color change occurred in patches indicating a non-homogeneous covering. The most successful method resulted in immersing a liquid nitrogen temperature film into the pure solvent followed by a misting of the catechol/dimethyl succinate solution. This increased thickness of the pure solvent caused by the dipping prevents the indicator chemical from reacting with the film. Dimethyl succinate was chosen for these tests since it has the highest melting point of the cold temperature solvents, and therefore, is easiest to study. The use of sprays and immersions to coat the slide caused the frozen solvent to render the sensor opaque to the Perkin Elmer Lambda 3A UV/Vis spectrophotometer. Therefore, it was necessary to determine a method of removing the opaque solvent layer to allow a UV/Vis spectrophotometer measurement of the film.

4.1.2 *Cleaning and Quenching*

Attempts to clean the film surface included physical wiping, rinsing with RO water, and rinsing with 50% by volume ethanol and water. Studies were done with both frozen slides and slides above the melting point of the diethyl fumarate (1-2°C) solvent. The slides were allowed to react for approximately 30 minutes to produce a visible color change. One half of the slides were frozen and cleaned. The other one half were immediately cleaned of the liquid solvent. Additionally, two slides were kept without cleaning for a reference. Cleaning of the frozen slides was accomplished by first knocking the frozen solvent layer off of the slide followed by cleaning by wiping with a Kimwipe@, rinsing with RO water, or rinsing with 50%(vol.) ethanol and RO water. The films in the liquid solvent were also cleaned by these methods. Results show that any rinsing of the slide causes a loss of intensity by up to 50% compared to measurements obtained before rinsing. This loss of intensity may be caused by the replacement of the catechol that is attached to the titanium by water or ethanol since all of these species have an OH functionality. Use of other cleaning solvents without an OH group may not affect the intensity of the color change, but were not pursued due to the problems encountered in the quenching experiments discussed below. The cleaned sensors were monitored over 3 days. The intensities did not vary more than a few percent over this time indicating that the reaction may be quenched if cleaning of the slide is successfully performed. This implies that the sensor will be relatively stable after cleaning is performed.

Quenching studies were made using 98 ppm catechol in dimethyl succinate. The solvent was sprayed onto a liquid nitrogen cooled unreacted film and placed in a refrigerated water/ethylene glycol bath at -28°C for one day. The edges of the slides, after cleaning, showed a color change visible to the naked eye. The center of the films gave an absorbance reading of approximately 0.08. The appearance of a color that occurs on an unreacted film indicates that diffusion still occurs when the solvent is frozen and that the reaction will not quench even at temperatures approximately 50°C below the solvent's melting point. Therefore, a sensor of this type will not stay inactive and will not quench when returned to temperatures below the freezing point of the solvent.

4.1.3 *Results and Discussion*

Since the quenching studies indicated that the reaction proceeds after refreezing, it was decided to determine if this technique would work for high temperatures(65°C to 140°C). Therefore, only a few studies were conducted with the cold temperature sensor.

Experiments were performed to determine the reproducibility of the cold temperature sensors. Films were allowed to react for 30 minutes in 98 ppm catechol/dimethyl succinate solution at 30°C. The films were then frozen at a freezer temperature of -18°C for five hours. The slides were cleaned by physical removal of the frozen solvent and intensities measured. Results indicated reproducibility of the color intensities within 15% of the average.

Results of experiments to determine change in intensity as a function of concentration were carried out in two different solvents. Concentrations of catechol from 1 to 1000 ppm were studied in dimethyl succinate and diethyl fumarate at 32°C for approximately 3 days. Results of these experiments are shown in Figure 7 for dimethyl succinate and Figure 8, on the following page, for diethyl fumarate. The line fitting of these data points is by computer interpolation. The absorbance readings consist of the intensity at 440nm minus the background intensity at 620nm. Concentrations of catechol in dimethyl succinate lower than 10ppm could not be studied since the resulting intensity was less than 0.1 absorbance units. The results displayed in Figures 7 and 8, on the following pages, indicate that different concentrations of catechol will give different intensities as a function of time and may be used to customize sensors for specific applications.

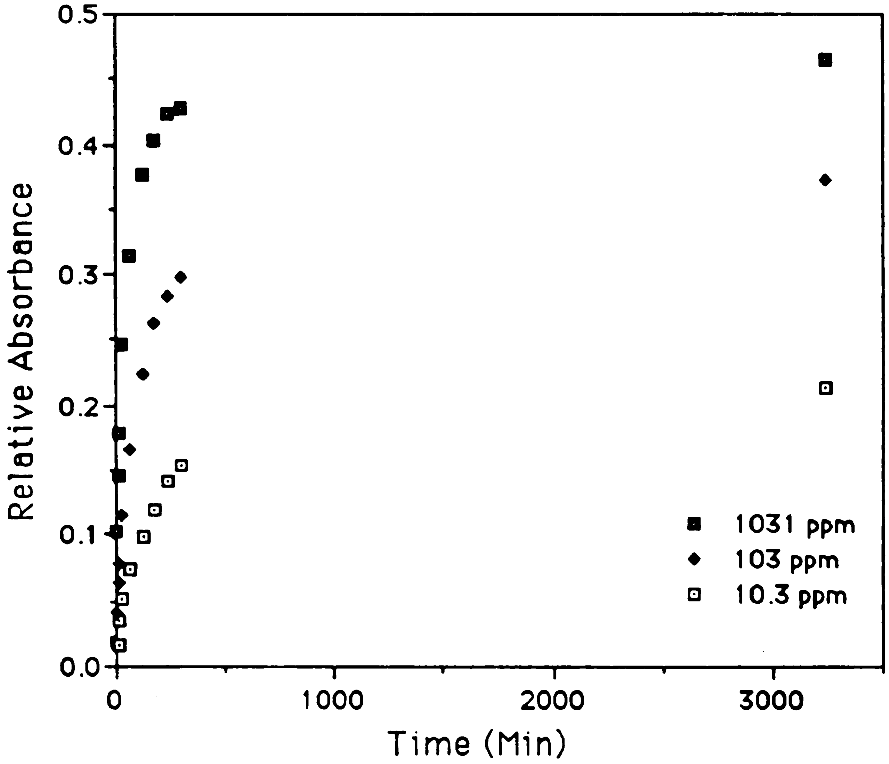


Figure 7 Relative absorbance-time profile of catechol/dimethyl succinate solution reacted with the titanium film at 32°C.

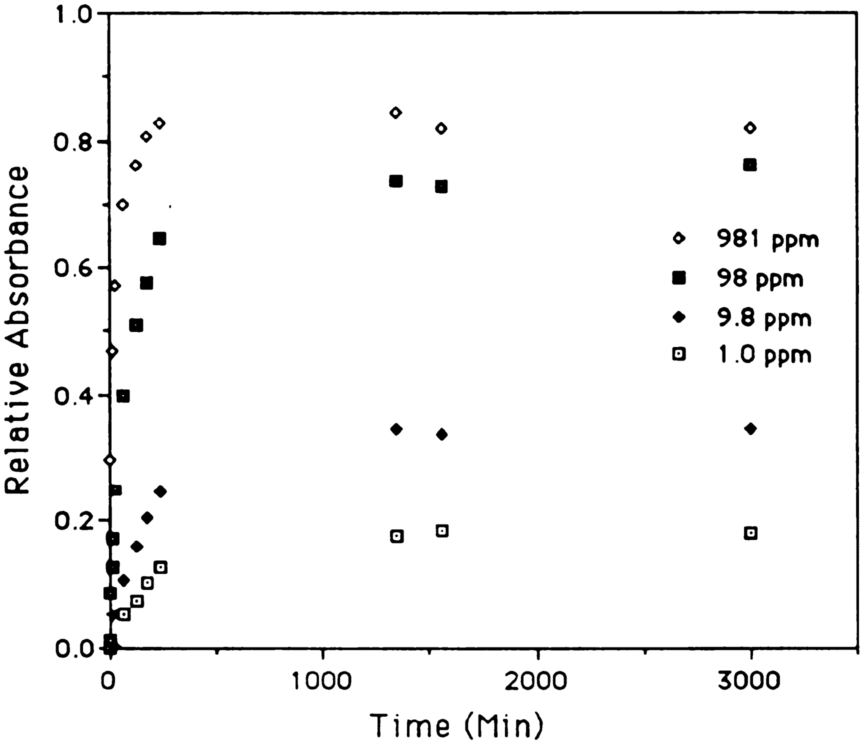


Figure 8 Relative absorbance-time profile of catechol/dimethyl fumarate solution reacted with the titanium film at 32°C.

To summarize the results of the cold temperature sensor, the construction materials were; catechol as the indicator and valeric acid based original preparation for the film. This resulting cold temperature sensor does not quench efficiently when returned to temperatures below the freezing point of the solvent. The absorbance intensity varies as a function of concentration and time as expected. The sensor requires a thick layer of frozen pure solvent followed by a misted layer of solvent and indicator chemical to prevent premature reaction. Therefore, the use of such devices would be appropriate only to indicate whether a particular temperature threshold was reached. Once this temperature threshold is reached, a visible reaction is quickly apparent. This reaction occurs rapidly due to the fast melting of the thin layer of solvent allowing almost immediate reaction between the indicator chemical and the film layer. However, the length of exposure could not be reliably determined since the reaction proceeds beyond refreezing. For this reason, no further kinetic analysis was performed on the cold temperature system.

4.2 Elevated Temperature Sensor

4.2.1 *Construction and Materials*

The construction of an elevated temperature range (65°C to 140°C) sensor, like the cold temperature range sensor, involved first determining the appropriate materials. This section of research was conducted after new film preparation techniques were developed by Torgerson as discussed in section 3.1, and therefore, the investigation was pursued utilizing these new films. Most of the chemicals listed in Figure 5 were allowed to react with both the valeric and valeric/lauric based films at 65°C for up to five hours. The solvent used for these studies was 1ml of paraffin (Gulf®) wax containing 0.5M to 1M of the indicator chemicals. This study indicated that the valeric/lauric based film produced intensities equal to, or greater than, the valeric based film. Therefore, we determined that the valeric/lauric based film (new preparation) would be used for the remainder of this study. All thermal reactions for the elevated temperature sensor were carried out in a Fisher Scientific Isotemp® Programmable Oven (Model 818F).

Continuing with the determination of the materials, qualitative measurements of the potential indicator chemicals was performed as described in the previous paragraph. Visual results including the solubilities, solution and film color changes are tabulated in Table 5. The goal of this qualitative research was to find an indicator that would react with the titanium to give an obvious color change within a reasonable amount of time as discussed in section 3.2. These results show that the most likely high temperature indicator would be found from the catechol-like compounds. These compounds are colorless in solution and react well with the film producing a color change.

The most successful chemicals of the qualitative studies shown in Table 5 were used for a more quantitative experiment to determine the most suitable chemical to use with this high temperature (65°C to 140°C) film. Some additional chemicals not listed in Table 5 were also included in this study. These additional chemicals were included based on the similarities between these chemicals and the most qualitatively effective chemicals, the catecholates. These additional chemicals are illustrated in Figure 5. This quantitative study was done by evaluating the reaction intensity, reaction kinetics, and the quenching performance of the colorimetric reaction. The compounds were dissolved in approximately 2ml of melted paraffin wax at a temperature of 65°C. Excess indicator was added to the melted wax and allowed to sit overnight at 65°C to ensure saturation and equilibrium. Valeric/lauric acid based film coated slides were immersed in the 65°C wax solutions for periods of 5, 10, 15, 30, 45, and 60 minutes. The wax solutions were placed in a water bath at 65°C to ensure thermal stability. Films removed from the wax solution were hand shaken to remove the excess wax from the slide. Absorbance of the

Table 5 Qualitative determination of indicator chemicals for the high temperature sensor.

Titanium film reaction in paraffin wax at 65°C for five hours

Chemical Name	Solution Color	Solubility in Wax	Reaction Color
EDTA	none	aprox. 1/2	none
Acac	yellow	2-phases	none
1,10 Phenanthroline monohydrate	none	partly	none
Pthalic Anhydride	none	partly	none
BHA	rusty-red	partly	rusty-red
Alizarin	yellow/ orange	partly	rusty red
Chrysin	pale yellow	partly	pale yellow
Esculetin	pale yellow	partly	none
Orcinol Monohydrate	pale yellow	mostly	yellow
P-Benzoquinone	yellow	partly	yellow
6,7-Dichloro-1,4-dihydroxylanthraquinone	cloudy rusty color	partly	light purple
2,5-Dichloro-3,6-dihydroxy-p-benzoquinone	red/orange	partly	red-purple
Juglone	yellow/ orange	partly	slight red
Lawsone	pale yellow	partly	pale yellow
Veratrole	none	2 phases	none
1,2-Naphthoquinone	dark	slightly	none
Tetrachloro-1,2-benzoquinone	red/orange	partly	yellow
Galangin	pale yellow	slightly	yellow
BHT	none	partly	faint yellow
Ascorbic Acid	none	partly	light yellow
3,4 Dihydroxy Benzoic Acid	none	partly	faint yellow
3,5 Dihydroxy Benzoic Acid	none	partly	faint yellow
Pyrogallol	none	partly	yellow
4-Methyl Catechol	none	partly	dark brown/red
Catechol	none	partly	dark yellow
Salicylic Acid	none	partly	pale yellow

film from 700 nm to 350 nm was recorded on the Perkin Elmer Lambda 3A UV/Vis Spectrophotometer in a polystyrene cuvette versus a blank film in a polystyrene cuvette. The difference in absorbance from 350 nm to 600 nm was calculated from the graphical output of the spectrophotometer.

Kinetics of reactions with the film were followed by determining the absorbance of one film that had been immersed in the wax solution for 5, 10, 15, 30, 45, and 60 minutes. Kinetic curves of absorbance versus time were plotted and used to give a qualitative estimate of the chemicals kinetic feasibility. An example of this type of plot is given in Figure 9. If the kinetic curve, plotted in this manner, had a smooth shape with the reaction taking at least 10 minutes before reaching a plateau, that chemical was determined to have good kinetic possibilities for further study. Chemicals that did not have this type of kinetic curve were categorized as poor.

The intensity of the reaction between the chemical and the film is the second criteria we used to determine the adequacy of the chemical. The difference in absorbance from 350 nm to 600 nm after 60 minutes of reaction is the basis for the intensity measurement. Relative intensities greater than 2.0 are categorized as high, and intensities less than 0.2 are categorized as low with other classifications distributed throughout the remainder of the range.

Quenching studies of the chemicals were done by reacting the films for 5, 10, 15, 30, and 60 minutes in the saturated wax solution and obtaining a baseline absorbance. The films' absorbances were then determined approximately five hours later and then again after 24 hours. The films were stored in the dark between readings. The change in absorbance compared to the baseline is the basis for the quenching evaluation. A good quenching classification resulted if the absorbance intensity did not vary more than approximately 10%

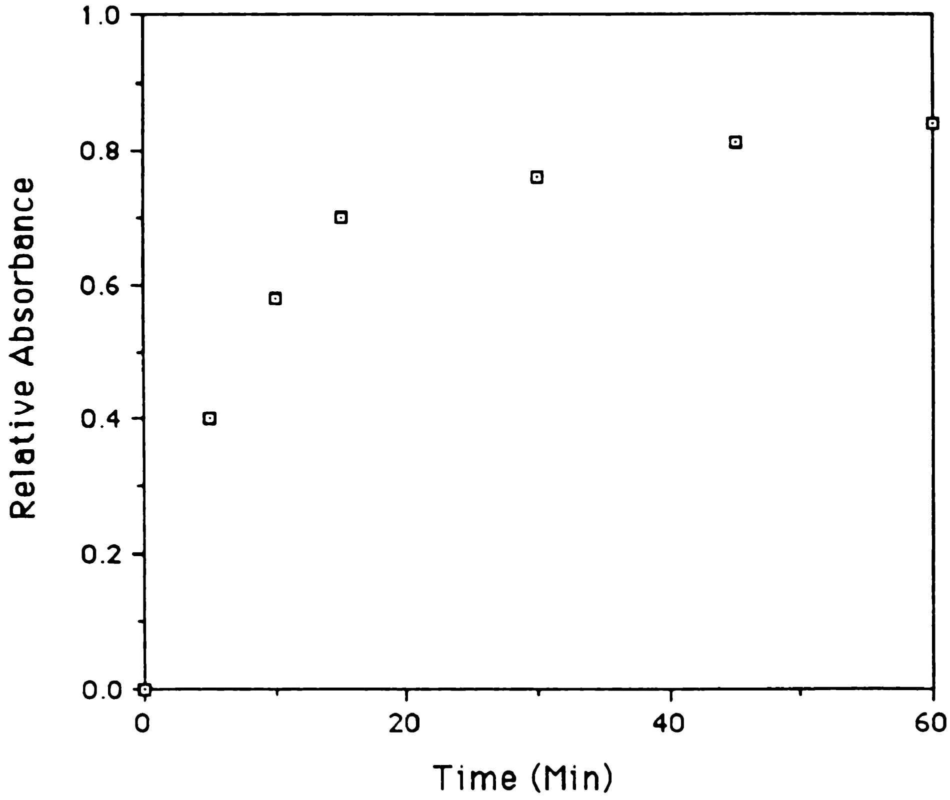


Figure 9 Kinetic results of catechol/paraffin wax solution reacted with titanium based film at 65°C.

absorbance over the initial value for a majority of the film samples. Other classifications were more arbitrary and were based on the changes in intensity after 24 hours compared to the baseline.

The results of the kinetic, intensity, and quenching feasibility studies on various chemicals are given in Table 6. Again, the chemical structure of these chemicals is illustrated in Figure 5. Some chemicals, like catechol, pyrogallol, and phenol were also studied in section 4.2.1. These compounds were repeated to determine if increased temperature would make these chemicals more suitable for indicators. Using the results in Table 6 it was decided that the chemicals for further study for the high temperature sensor would be: 4-methyl catechol, catechol, and methoxy catechol. All have good kinetic and intensity classifications with fair quenching results. It was decided that quenching was less important than kinetics and intensity since it is not likely that long delays would occur between the color change reaction and the measurement of these high temperature sensors. However, it was also decided that methoxy catechol has an

Table 6 Feasibility of indicator chemicals for high temperature sensors.

Chemical	Kinetics	Intensity	Quenching
N-Propyl gallate	good	low	poor
3-Methyl catechol	poor	poor	good
4-Methyl catechol	good	good	fair
BHA	good	good	poor
Tetracloro catechol	poor	good	good
Phenol	poor	low-poor	good
3,5 Di-t-Butyl catechol	good	fair	fair-good
Resorcinol	good	low	good
Catechol	good	good	fair
Methoxy catechol	good	high	fair

intensity that is too large(>2.00) for our purposes. This high intensity indicated that kinetic studies for times greater than 60 minutes would exceed the maximum instrument reliability of 3.00 absorbance units. Catechol was the chemical of choice for the high temperature sensor since it is readily available, inexpensive, and worked well in the low temperature studies. 4-methyl catechol may be a suitable chemical for temperature ranges greater than 150°C since it has a greater melting point than catechol.

The wax blends listed in Table 4 were chosen as the solvents for the high temperature sensor. These specific waxes are paraffin wax, IRM Hewax, and IRM #8618 wax. Qualitative tests of the solubilities of indicator chemicals in the wax blends indicated that sufficient amounts of indicator would dissolve in the wax to give a color change to the film. Therefore, since waxes are easy to work with and non-toxic, these wax blends were chosen as the solvent medium for the higher temperature sensor.

4.2.2 *Cleaning and Quenching*

Attempts were made to determine a method of removing the wax solvent layer from the high temperature sensor. This removal of the wax layer was desired to allow easier visual and UV-Vis Spectrophotometric analysis of the sensor. Rinsing with boiling water, wiping with a Kimwipe®, and freezing (10°C) the vial containing the wax and slide were methods attempted. Rinsing and/or wiping the slide caused a reduction of the color intensity. Freezing of the wax and physical removal of the slide was very difficult due to the breakage of the slide from the force required to remove the slide from the frozen wax containing vial.

Due to the problems encountered in removing the wax from the slides, the slides were cleaned upon removal from the indicator solution by vigorous shaking of the slide. When measurements were required, the slide was removed from the melted wax solution and physically shaken to remove most of the excess wax. Applying the bottom edge of the slide to an absorbent material such as a paper towel, assisted in the removal of the excess wax by capillary action. This method of cleaning was tested by briefly immersing previously reacted slides in a pure wax solution to build up thicker and thicker layers of wax, a method similar to candle making. Measurements of the background (600nm) and the colored band (350nm) were obtained after each successive wax coating. The relative color intensity did not appreciably vary until the third or fourth layer of wax was applied. Three or four wax layers produced a relatively thick wax coating compared to the wax thickness on the slides that resulted from the method of physical shaking discussed earlier. Therefore, it was concluded that this method of cleaning the slides, physical shaking, would be effective and allow easier visual and UV/Vis spectrophotometer measurements.

The quenching of the high temperature sensor was discussed in section 4.2.1. Since catechol was the indicator chemical used for this study, and based on data discussed in section 4.2.1, it appears that once the wax solution solidifies, the colorimetric reaction rate approaches zero and quenching of the sensor occurs.

4.2.3 *Results and Discussion*

Two brief variations on the construction of a high temperature sensor were attempted. The first was the addition of a zirconium film layer on top of the titanium film layer. It was believed that a layer of zirconium based film would provide a diffusion barrier to the indicator, thus allowing a longer reaction time. Also, it was determined that zirconium films do not react with catechol as does titanium films. A coating of the zirconium film solution was placed over a valeric/lauric new preparation film. These two layer films were reacted for one hour in four different indicator chemicals of approximately 0.5M concentration that were dissolved in paraffin wax at 65^{o}C. Comparisons were made of the zirconium coated sensors to valeric/lauric film sensors. Visual observation of these sensors indicated that the films with an extra coating of zirconium produced slightly darker color changes in reactions with catechol and 4-methyl catechol solutions. This indicates that the reaction rates are increased with the addition of a zirconium film layer. Reactions with orcinol and salicyclic acid solutions did not produce any appreciable change in intensity.

An additional experiment was performed using basic (pH>7) solvent solutions and basic film preparation solutions. This experiment was performed to determine if pH would affect the colorimetric reaction in the hope that the color would shift from yellow to a more visible color such as red. Reactions were carried out on valeric/lauric films reacting with 0.11g catechol dissolved in 1ml of paraffin wax. The wax solution was made basic with the addition of NaOH pellet of approximately 0.08g. These reactions produced a more intense color change when compared to a neutral solution. The excess non-dissolved catechol becomes green-black colored on contact with the NaOH indicating possible degradation of the catechol. Film solutions with a pH greater than 7 were prepared by using a valeric based film solution with approximately 0.08g of NaOH added after addition of the water. The films prepared by this method did not produce a homogeneous covering when spin-casting was attempted. Films prepared from this solution were reacted with four indicator chemicals in paraffin wax at 65°C for 5 hours. 4-methyl catechol and catechol indicators produced a non-homogeneous color change (dark red/brown and yellow/orange, respectively). Reactions with salicylic acid and 6,7-dichloro-1,4-dihydroxy anthraquinone produced more uniform colors of yellow and light purple, respectively. These experiments were not pursued since an increase in color intensity would cause a corresponding decrease in reaction time and the measuring lifetime of the sensor.

Kinetic studies were performed on the three wax blends at various temperatures above their melting points. Catechol was added to the melted waxes in excess and allowed to equilibrate overnight. Initial experiments with paraffin wax used the supernatant as the solution and are described as unsaturated experiments. Later experiments used the catechol-wax solution supernatant with the addition of a few crystals of catechol to ensure the constant concentration of the solution during the kinetic run and are labeled as saturated solutions. The temperatures studied were: 65, 85, and 95°C for paraffin wax (melting range 51-53°C); 90, 100, 110, and 120°C for the IRM #8618 wax (melting range of 80-84°C); 120 and 130°C for the IRM Hewax (melting range of 110-118°C). The reactions were monitored for up to 5 hours with measurements generally taken at 5, 10, 15, 30, 45, 60, 150, 240, and 300 minutes after the reaction was initiated. The reaction was initiated by the addition of a film-covered glass slide to the vials containing the catechol/wax solution at the desired reaction temperature. Two types of blank slides were also measured for all time and temperatures. These blanks consisted of film coated slides immersed in pure wax solutions, and also as clean slides immersed in the catechol-wax solution. An example of the data collected for one sample at one temperature at a specific time is shown in Figure 10 on the following page.

An example of the completed data generated by these experiments is shown in Figure 11, two pages following. This is a plot of the relative absorbance of the colored film product of the IRM#8618 wax/catechol solution reacted at 100°C averaged over all of the experimental runs. The relative absorbance is the difference between the absorbance intensity at 350nm (colored region) from the intensity at 600nm (background region) as measured by the Perkin-Elmer lambda 3A UV/Vis spectrophotometer. Calculation of absorbance using relative values is required to eliminate the errors that may result from measuring the intensity through a variable thickness of the solidified wax solution.

Analysis of the data generated by these experiments was attempted using various models. This analysis was desired in the hope that useful calibration curves suitable for industrial application would be found. This data reduction was also used to attempt to eliminate and reduce the inherent errors and scatter of using a UV/Vis spectrophotometer (designed for solutions) on solid wax covered films. These errors in readings may result in a very

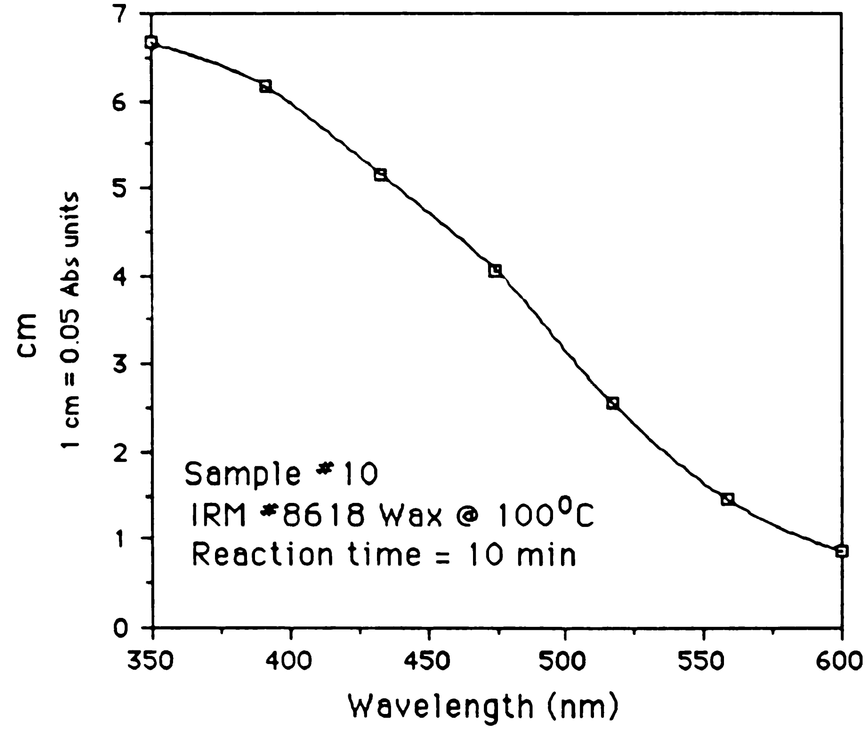


Figure 10 Absorbance versus wavelength for catechol/IRM #8618 wax solution reacted at 100°C for 10 minutes.

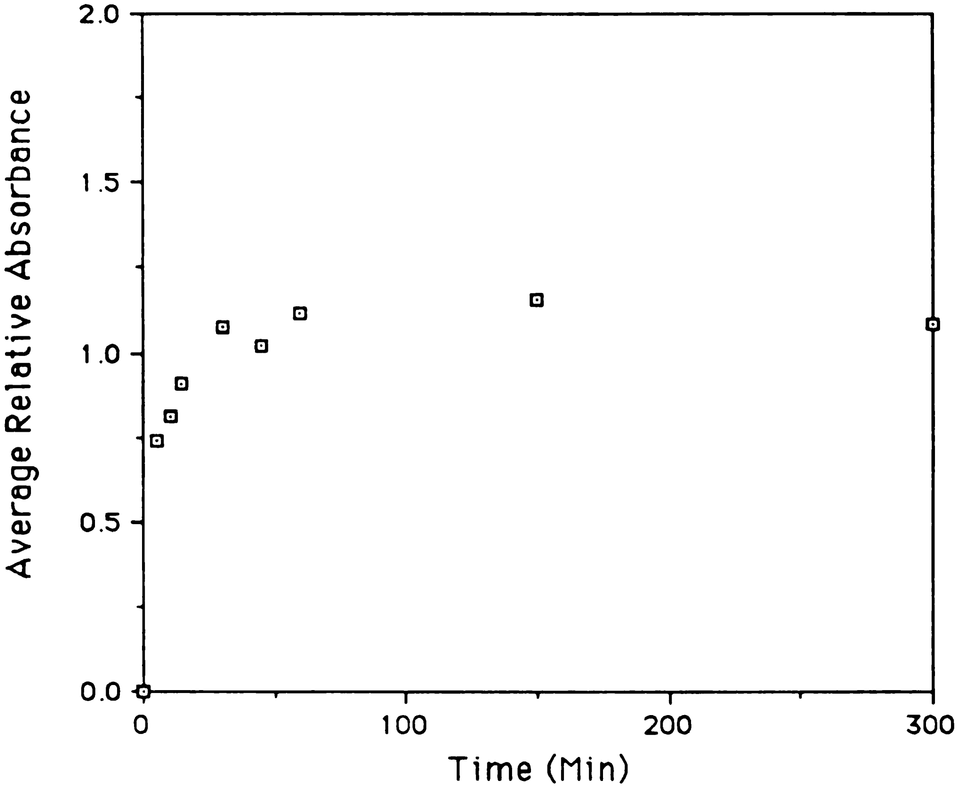


Figure 11 Average absorbance of the colored film product of the catechol/IRM#8618 wax solution reacted at 100°C.

large spread of data points when individual runs are examined and compared. Plots of the absorbance versus time for individual runs were examined and indicated that data reduction by some method should be attempted to condense the range of values determined by the experiments. An example of this spread in data from individual runs is shown in Figure 12, on the following page. This figure includes interpolated curves which are shown by the lines in the figure. The large spread in the data illustrate a reason for the data reduction procedures and analysis.

The raw data used for this following analysis is included in the appendix as Tables A-1 to A-3.

The data analysis method assumes that there are a constant and set number of reaction sites in the film. This is assumed since the catechol reacts with the titanium center incorporated in the film. When the catechol reacts with the titanium site, this site is assumed to become inactive with respect to further reaction. Using the chemical reaction shown in equation 1, a kinetic rate expression

$$\text{Catechol} + \text{Titanium Site} \dashrightarrow \text{Colored Complex} \qquad \text{(eq. 1)}$$

can be constructed. Using the variables C for catechol, S for the non-reacted site, and P*S for the colored complex product it is possible to derive the following expressions. Using the rate of change of the available sites and assuming that this is first order with respect to the number of open sites gives equation 2.

$$\frac{-dS}{dt} = k^*[C]^*[S] \qquad \text{(eq. 2)}$$

The variable k in equation 2 is the rate constant. Assuming that the concentration of the catechol is much greater than the number of active sites, and therefore, approximately a constant will reduce equation 2 to equation 3 where k' is a pseudo-first order rate

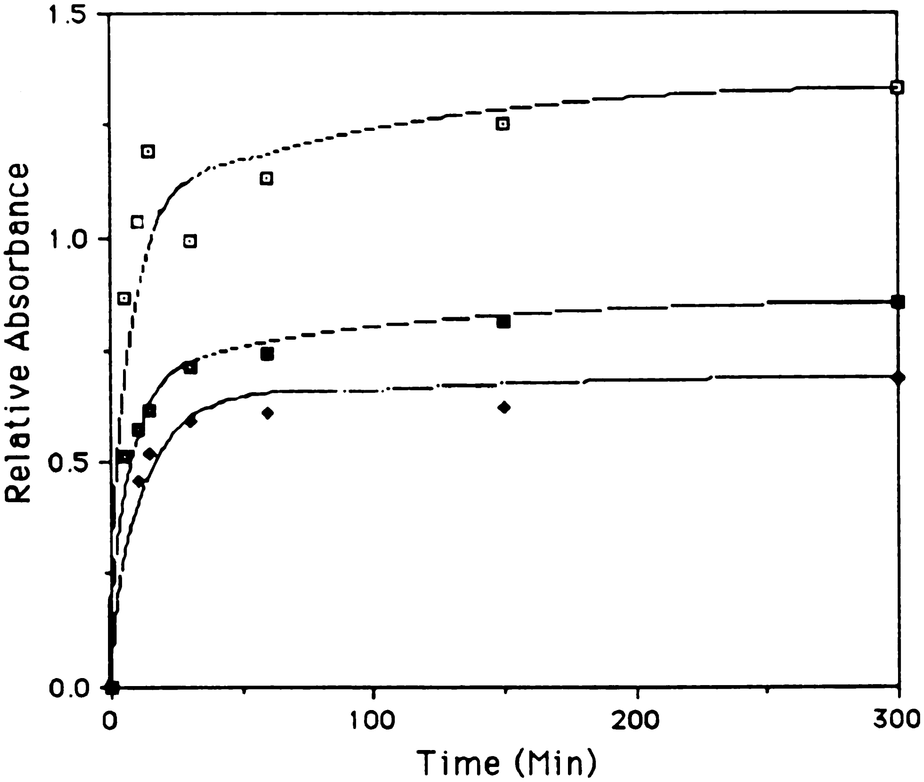


Figure 12 Absorbance of film product vs. time for three catechol/paraffin wax solution runs at 65°C.

constant. Rearranging and integrating equation 3 using the limits

$$\frac{-dS}{dt} = k' * [S] \qquad \text{(eq. 3)}$$

of S_o to S as time goes from 0 to t results in equation 4. S_o is the maximum and original number of open sites available in the film. The variable S can be derived by a mole balance between the total

$$S = S_o * \exp(-k't) \qquad \text{(eq. 4)}$$

number of sites and the number of sites that have reacted with the catechol and have become inert. This relation given in equation 5 assumes the number of open sites(S) is equal to the number of

$$S = S_o - [P^*S] \qquad \text{(eq. 5)}$$

total sites(S_o) minus the number of sites reacted and made inert($[P^*S]$). Substituting equation 5 into equation 4 to eliminate S results in equation 6. This equation shows that the colored

$$[P^*S] = S_o *\{1 - \exp(-k't)\} \qquad \text{(eq. 6)}$$

complex ($[P^*S]$) that is measured by the UV/Vis spectrophotometer is exponentially related to time and proportionally related to the maximum number of reaction sites in the film. This relationship was used to least-squares fit the data determined by experiments. To reduce the amount of data and to help eliminate errors discussed above, the individual runs were averaged before being fit to equation 6. Averaged data for the various waxes and temperatures are given in Table 7, on the following page.

The data in Table 7 was fitted to equation 6 using a least squares routine from Kalida Graph with a Macintosh computer.

Table 7 Average relative absorbance of film product data reacted in catechol/wax solutions at studied temperatures.

Paraffin Wax

Time (Min)	65°C Saturated	65°C Unsat	85°C Saturated	85°C Unsat	95°C Saturated
0	0.000	0.000	0.000	0.000	0.000
5	0.597	0.661	0.588	0.391	0.855
10	0.600	0.702	0.635	0.526	1.200
15	0.633	0.765	0.680	0.502	1.280
30	0.639	0.790	0.732	0.579	1.345
45	0.677	NA	NA	NA	1.265
60	0.701	0.863	0.825	0.608	1.380
150	0.755	0.961	0.880	0.667	1.410
300	0.770	0.973	0.944	0.627	1.540

IRM Waxes

Time (Min)	90°C #8618	100°C #8618	110°C #8618	120°C #8618	130°C Hewax
0	0.000	0.000	0.000	0.000	0.000
5	0.426	0.474	0.772	0.754	0.510
10	0.570	0.815	1.012	0.826	0.490
15	0.619	0.908	1.047	0.910	0.723
30	0.696	1.079	1.122	0.875	0.850
45	0.700	1.020	1.096	0.745	0.626
60	0.707	1.115	1.031	0.858	0.870
150	0.767	1.158	1.273	0.938	0.640
300	0.790	1.082	1.136	0.843	0.498

Figures 13, 14, 15, and 16, on following pages, depict the fit of the data for experiments with saturated paraffin wax solution, unsaturated paraffin wax solutions, IRM #8618 wax, and IRM Hewax, respectively.

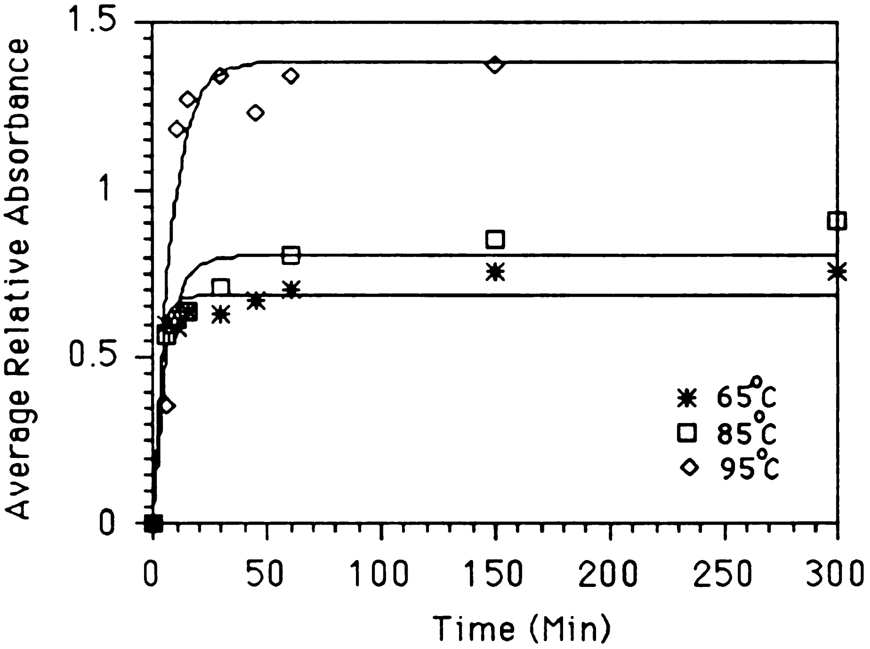


Figure 13 Average relative absorbance and least squares data fit of titanium film product reacted in catechol/saturated paraffin wax for all temperatures studied.

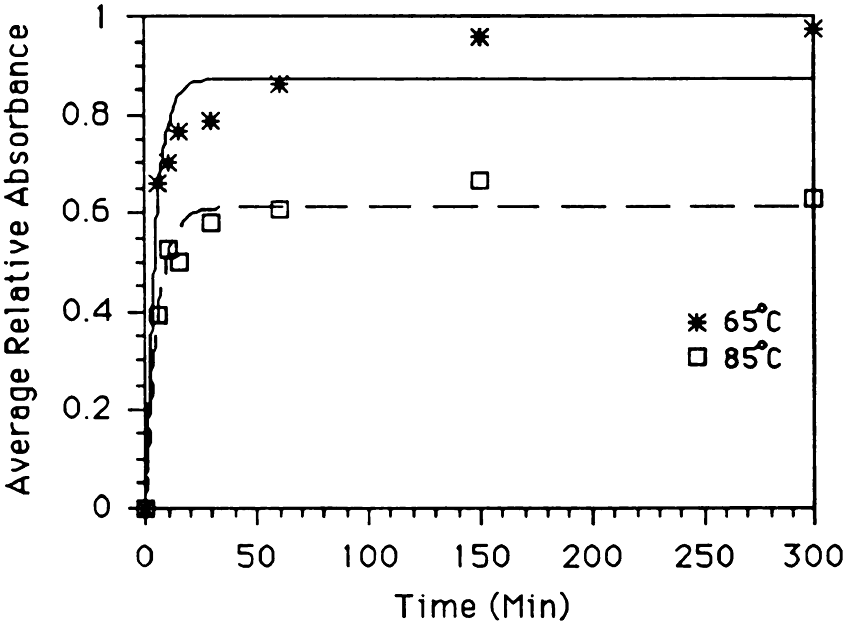


Figure 14 Average relative absorbance and least squares data fit of titanium film product reacted in catechol/unsaturated paraffin wax for all temperatures studied.

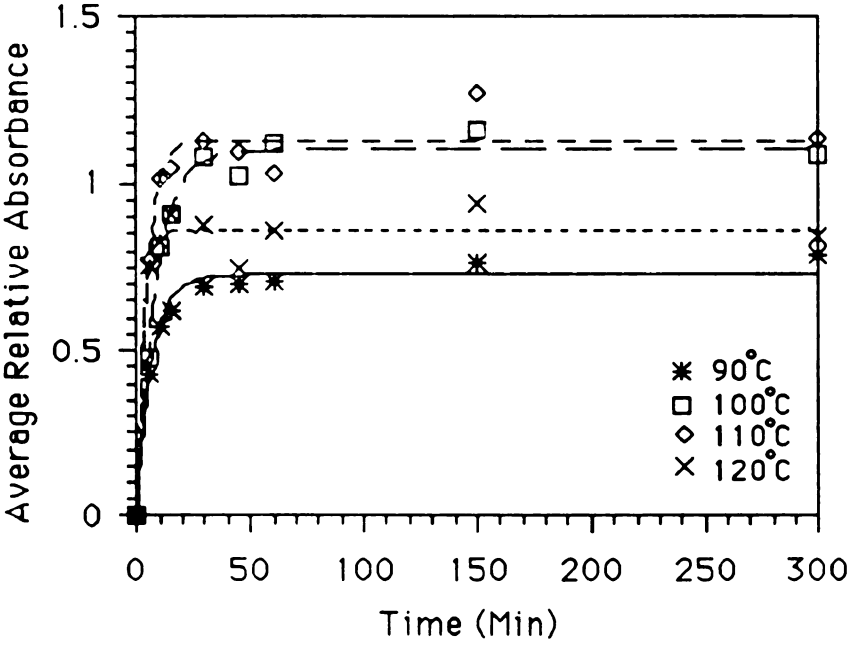


Figure 15 Average relative absorbance and least squares data fit of titanium film product reacted in catechol/IRM #8618 wax for all temperatures studied.

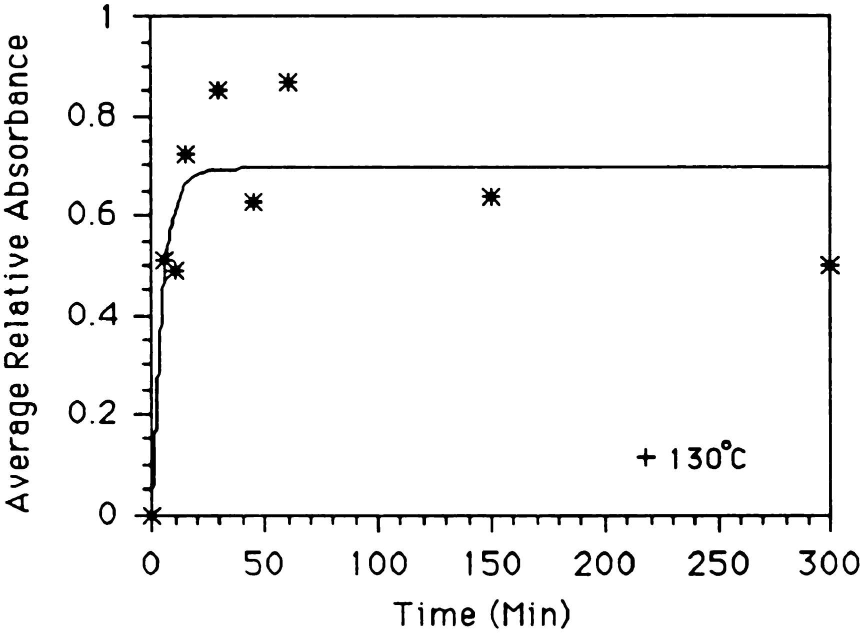


Figure 16 Average relative absorbance and least squares data fit of titanium film product reacted in catechol/IRM Hewax for all temperatures studied.

The values produced for k' and for S_0 from the graphs are tabulated in Table 8.

Table 8 S_0 and k' results of fit.

Wax	Temp(°C)	S_0(Ave Abs)	k'(Min^{-1})	Correlation
Paraffin Sat	65	0.689	0.347	0.973
Paraffin Sat	85	0.827	0.179	0.959
Paraffin Sat	95	1.380	0.191	0.961
Paraffin Unsat	65	0.874	0.219	0.979
Paraffin Unsat	85	0.611	0.182	0.990
IRM #8618	90	0.729	0.154	0.994
IRM #8618	100	1.098	0.122	0.951
IRM #8618	110	1.126	0.225	0.836
IRM #8618	120	0.858	0.415	0.839
IRM Hewax	130	0.694	0.210	0.961

Examination of the data does note lead to any conclusions based on numerical trends. Also, S_0 can not be related directly to any physical constant since the absorbance is an indirect measurement of the colored complex concentration. S_0 is related to the total number of sites available for reaction and should be relatively constant throughout all the temperatures and waxes. This consistency results from the film being of a constant thickness, consistent preparation, and constant beam area in the UV/Vis spectrophotometer. With this constant volume being measured and consistent film stoichometry, the number of available sites should remain as a constant.

Using these results for the k' values allows the calculation of the activation energy using the Arrehenius equation which is linearized in equation 7. A plot of the ln(k') versus 1/T results in

$$\ln(k') = \ln(A) - \frac{E_a}{R * T} \qquad \text{(eq. 7)}$$

Figure 17 for the IRM #8618 data points. This graph has two best fit lines added to show the agreement of theory to data. One line uses all four data points for this wax while the other line does not use the 90°C data point for IRM #8618 wax. As the graph illustrates, the fit is much better without this data point. This may be caused by the reaction taking place near to the melting point of the IRM #8618 wax(MP=80 to 84°C). This may have resulted in problems due to the time taken for the excess wax on the slide to liquefy when the slide was reinserted into the liquid wax solution. This lag between the start of the reaction and the insertion of the slide into the wax solution, in effect, would increase the effective rate constant. This arises if the rate constant is expressed as the reaction rate divided by the reactant concentration. With the delay in melting occurring, the visible concentration of reactants is effectively reduced causing the rate constant to increase. This increased rate constant when converted to the Arrhenius equation by the natural log would tend to decrease the ln(k') value as seen in Figure 17, on the following page.

Using the slope and intercept values given in Figure 17 for the calculation of the activation energy(E_a) gives values of 1.08 KJ/mol for the data incorporating all points and 0.607 KJ/mol for the data that excludes the 90°C point.

Figure 18, on the second page following, is a Arrhenius plot of the paraffin wax saturated and unsaturated samples. This plot also shows that the low temperature samples(65°C) appear to have a increased k' value and decreased ln(k') value possibly caused by the reaction occurring near the melting point of the wax as discussed above. Since only three points were found for the saturated paraffin

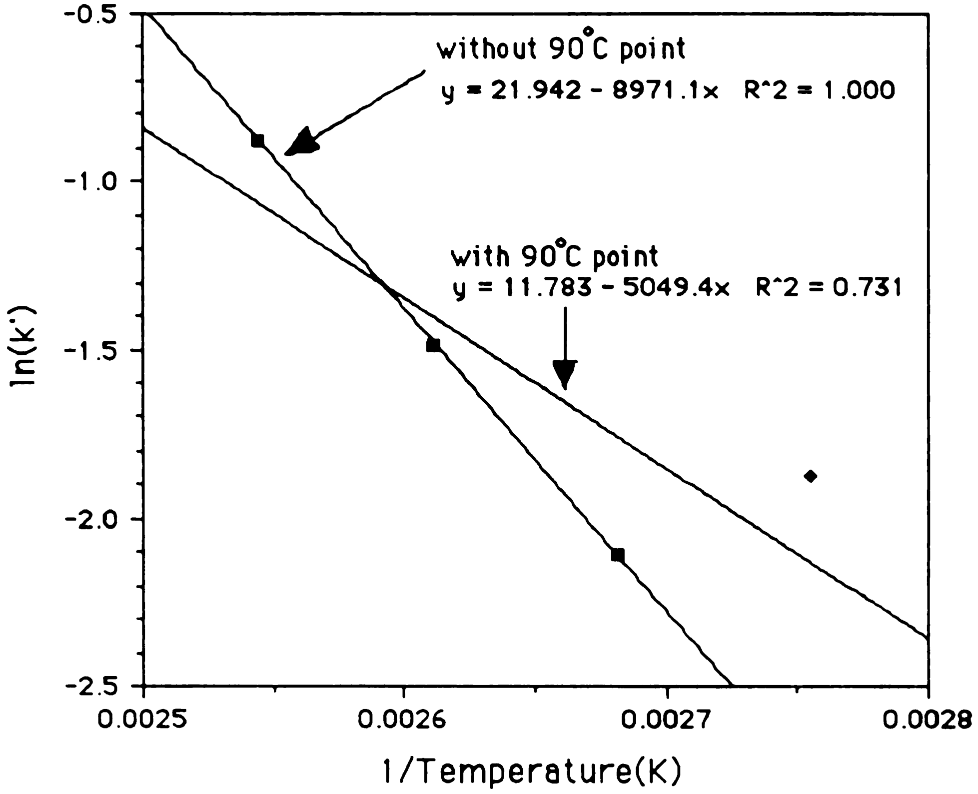


Figure 17 ln(k') versus 1/T from titanium film reacted with catechol/IRM #8618 wax solution.

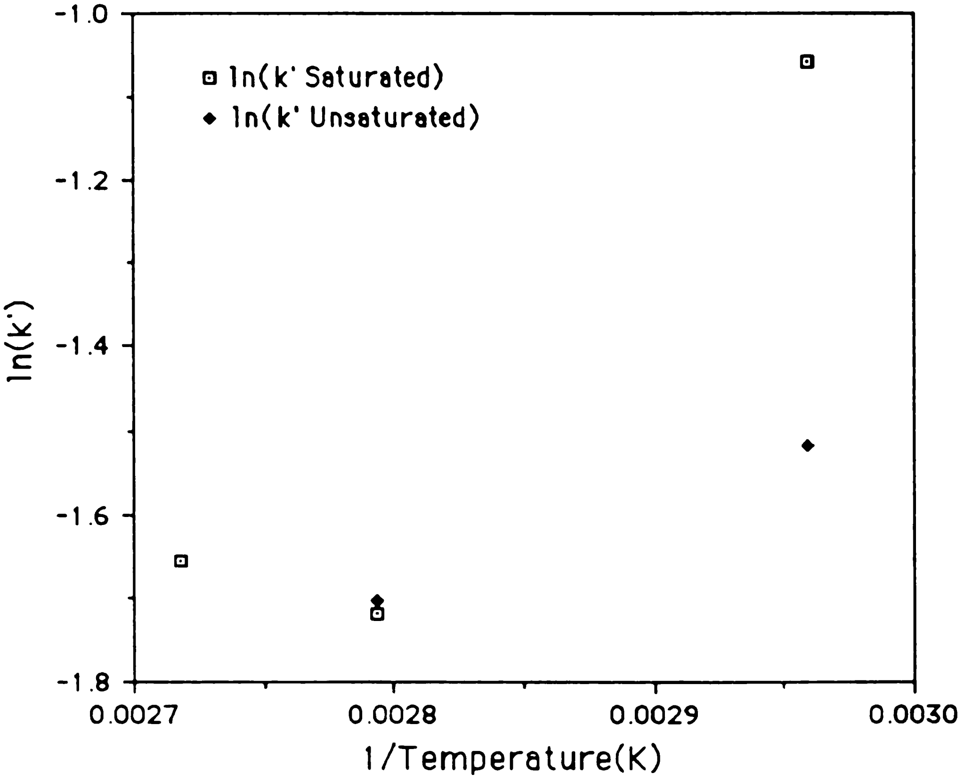


Figure 18 ln(k') versus 1/T from absorbance of titanium film reacted with catechol/paraffin wax data fitting.

wax reactions, no observations on trends can be observed. Also, for the unsaturated paraffin wax solutions, only two points are plotted and again no generalizations can be made.

To summarize, this analysis is based on a number of available sites for reaction in the film. This theory allows the calculation of a constant maximum number of sites for the films. Analysis of the data using the kinetic model results in values for this maximum number of sites that do remain relatively constant over all conditions. This model also allows calculation of a pseudo-first order rate constant and subsequent calculation of the activation energy. Paraffin wax samples do not give very good agreement of activation energy between expected and experimental and a possible explanation of this is discussed above. The IRM #8618 wax does give reasonably good results for the rate constant and activation energy. IRM Hewax was not analyzed since only one data point wax taken.

5. CONCLUSIONS

The purpose of this study was to determine the feasibility of using a film-based sensor for time-temperature history profiles. A titanium-based film was used as a colorimetric recorder of the time-temperature history of the ambient environment. This film would react with indicator chemicals dissolved in a frozen solvent. As the solvent reaches its melting point, reaction between the indicator and film would begin causing a color change of the film. Studies were performed on both low (-20 to 30°C) and high (65 to 140°C) temperature sensors.

Optimization of the film construction and indicator chemicals was performed for both temperature ranges. Catechol was the indicator chemical of choice for both temperatures. A valeric/lauric acid based titanium solution appears to be the most effective at producing a film for both temperature regimes. Solvents for the low temperature region that were used include dimethyl succinate and diethyl fumarate, while different wax blends were utilized for the high temperature region.

Studies were made on the feasibility of the low temperature sensor with indications that the colorimetric reaction would not quench upon return to temperatures below the freezing point of the solvent. This low temperature sensor may be useful as an indicator that the ambient environment has achieved a temperature above the freezing point of the solvent. This deficiency of the sensor caused a shift in emphasis to the high temperature sensor. The food industries need for a high temperature sensor and the already available low temperature sensors supported this shift.

High temperature sensors were studied using various wax blends from temperature of 65°C up to 140°C. Temperatures above 120°C caused rapid saturation of the spectrophotometer readings.

Analysis of this data was performed using a saturation type rate analysis using the number of titanium reaction sites as the limiting reactant. This model allowed line fitting of the experimental data with good results for the catechol/IRM #8618 wax solutions reacted to the titanium film. Absorbance values of the colored film were least square fitted using this model and allowed calculation of the effective rate constant and also a value proportional to the total number of available titanium centers in the film.

Quenching studies of the high temperature sensor indicate that the reaction does not proceed appreciably below the freezing point of the wax solvent. Use of the calculated data produced by the saturation model analysis could allow the integration of the recorded values from multiple melting point solvent sensor strips. This integration of the sensor readings would be used to determine the time-temperature history of the environment. Although, initial data curves are available in this paper, refined data should be obtained from any manufactured sensors produced in the future to take into account the manufacturing process and completed construction. Also formulas need to be developed to relate a possible changing thermal profile to the absorbance readings of the sensors.

In summary, the low temperature (-20 to 30°C) sensor studied will provide maximum ambient temperature information with the use of the appropriate solvents. The high temperature (65 to 140°C) sensor appears to be effective at determining the time-temperature profile of the steady-state surroundings and further research is needed to analyze the sensor readings to changing thermal conditions.

6. RECOMMENDATIONS FOR FUTURE WORK

Use of a cold temperature sensor appears feasible for determination of the maximum temperature of the environment. More study on this device should be performed if an application for this type of sensor is determined. Methods of construction that would permit the sensor to remain in the inactivated state must be determined. Different concentrations of the indicator and the use of different indicators should also be studied to allow more precise measurements. Different concentrations and indicators may allow this sensor to be converted to a true time-temperature device.

The high temperature sensor requires a more complete study on the kinetics of the indicator at different temperatures. Additional indicators and solvents should be determined to extend and define this high temperature range. If manufactured sensors are produced, these sensors should be tested to determine and refine the calibration curves as discussed in section 4. Experiments should be performed to confirm or disprove an accurate time-temperature measurement compared to the changes in the actual thermal environment. Mathematical models are available to determine the time spent by the indicator in various temperature ranges as a function of the reaction extent and reaction start temperature. These models should be compared to this sensor to confirm a method of determining the time-temperature profile over changing temperatures for various times.

7. APPENDIX: RAW DATA

Table A-1 Raw data of the absorbance of titanium film colored product reacted in catechol/paraffin wax solution.

Paraffin Wax @ 65°C Saturated

Absorbance

Time(Min)	# 1	# 2	# 3
0	0.000	0.000	0.000
5	0.540	0.615	0.645
10	0.480	0.660	0.660
15	0.591	0.615	0.705
30	0.552	0.660	0.705
45	0.615	0.645	0.771
60	0.690	0.675	0.740
150	0.735	0.750	0.780
300	0.630	0.810	0.870

Paraffin Wax @ 65°C Unsaturated

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.611	1.700	0.802	0.865	0.513	0.512
10	0.655	1.995	0.785	1.039	0.458	0.571
15	0.664	2.962	0.835	1.193	0.516	0.616
30	0.698	NA	0.963	0.994	0.589	0.708
60	0.854	NA	0.979	1.131	0.607	0.742
150	0.922	NA	1.197	1.253	0.621	0.811
300	0.939	NA	1.062	1.330	0.678	0.858

Paraffin Wax @ 85°C Saturated

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.645	0.439	0.615	0.782	0.617	0.427
10	0.643	0.470	0.613	0.854	0.721	0.510
15	0.736	0.438	0.569	1.013	0.729	0.592
30	0.789	0.561	0.736	0.981	0.737	0.587
60	0.788	0.694	0.913	1.028	0.840	0.689
150	0.987	0.657	1.079	0.872	0.955	0.731
300	0.957	0.681	1.188	0.881	1.129	0.829

Table A-1 (cont'd)

Paraffin Wax @ 85°C Unsaturated

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.555	0.443	0.379	0.364	0.467	0.141
10	0.617	0.510	0.660	0.440	0.705	0.223
15	0.657	0.527	0.497	0.479	0.562	0.293
30	0.693	0.565	0.798	0.532	0.481	0.405
60	0.738	0.603	0.560	0.635	0.608	0.501
150	0.754	0.614	1.000	0.567	0.541	0.527
360	0.803	0.685	0.585	0.577	0.553	0.556

Paraffin Wax @ 95°C Saturated

Absorbance

Time(Min)	# 1	# 2	# 3
0	0.000	0.000	0.000
5	1.080	0.150	1.335
10	0.990	1.350	1.260
15	1.230	1.185	1.425
30	1.230	1.455	1.350
45	1.050	1.545	1.200
60	1.110	1.380	1.650
150	1.170	1.740	1.320
300	1.230	1.590	1.800

Table A-2 Raw data of the absorbance of titanium film colored product reacted in catechol/IRM #8618 wax solution.

IRM #8616 wax @ 90°C

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.660	0.750	1.080	0.450	0.450	0.420
10	0.660	0.750	1.170	0.600	0.660	0.390
15	1.260	0.530	1.260	0.600	0.600	0.540
30	0.700	0.960	1.110	0.570	0.630	0.600
45	0.900	0.660	1.320	NA	NA	NA
60	1.290	0.720	0.810	0.570	0.690	0.660
150	1.170	0.690	1.470	0.660	0.810	0.660
300	0.930	0.660	1.500	0.690	0.840	0.750

IRM #8618 Wax @ 90°C (cont'd)

Absorbance

Time(Min)	# 7	# 8	# 9	#10	#11	#12
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.000	0.000	0.000	0.255	0.450	0.600
10	0.240	0.420	0.150	0.690	0.600	0.510
15	0.300	0.330	0.150	0.750	0.690	0.420
30	0.330	0.480	0.540	0.840	0.630	0.960
45	NA	NA	NA	0.330	0.750	1.260
60	0.570	0.600	0.570	0.720	0.840	0.450
150	0.720	0.420	0.870	0.780	0.960	0.000
300	0.720	0.450	0.870	0.750	0.900	0.420

IRM #8616 wax @ 100°C

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	1.590	1.080	1.170	0.900	0.390	1.080
10	1.470	1.200	0.930	0.390	0.330	1.260
15	1.680	1.200	1.470	0.630	0.600	1.320
30	2.318	1.260	1.140	0.360	0.360	2.052
45	1.620	1.530	1.170	1.470	0.600	1.750
60	1.590	1.500	1.230	0.330	0.450	2.336
150	1.710	1.500	1.200	1.170	0.570	1.710
300	1.770	1.590	1.320	0.270	0.510	1.943

Table A-2 (cont'd)

IRM #8618 Wax @ 100°C (cont'd)

Absorbance

Time(Min)	# 7	# 8	# 9	# 10	# 11	# 12
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.150	0.270	0.660	0.480	0.150	0.960
10	0.330	0.540	0.870	0.720	0.720	1.020
15	0.420	0.810	0.780	0.870	0.150	0.960
30	0.540	1.200	1.080	1.050	0.930	0.660
45	0.510	1.126	0.510	1.080	0.660	0.210
60	1.170	1.080	1.110	1.050	0.930	0.600
150	1.294	1.320	0.600	1.110	0.840	0.870
300	0.960	1.170	0.750	1.140	0.960	0.600

IRM #8616 wax @ 110°C

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.900	1.320	1.350	0.840	0.765	1.200
10	0.960	1.170	1.650	1.080	1.020	1.530
15	1.020	1.080	1.470	1.080	NA	1.650
30	1.155	1.215	1.710	1.230	NA	1.723
45	1.380	1.170	1.590	0.810	NA	1.830
60	1.200	0.780	1.830	1.080	NA	1.710
150	1.830	0.870	1.710	1.050	NA	4.850
300	1.800	0.570	1.862	1.100	NA	2.154

IRM #8618 Wax @ 110°C (cont'd)

Absorbance

Time(Min)	# 7	# 8	# 9	# 10	# 11	# 12
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.570	0.090	0.750	0.630	0.120	0.720
10	0.930	0.780	1.020	0.720	0.390	0.900
15	0.810	0.990	0.750	0.900	0.810	0.960
30	1.110	0.870	1.350	0.930	0.120	0.930
45	0.540	1.260	1.440	0.930	0.120	0.990
60	0.990	1.080	0.930	0.690	0.090	0.960
150	0.480	0.810	0.600	0.570	0.210	1.020
300	0.570	0.840	0.960	1.230	0.210	1.200

Table A-2 (cont'd)

IRM #8616 wax @ 120°C

Absorbance

Time(Min)	# 1	# 2	# 3	# 4	# 5	# 6
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.765	1.200	0.840	1.050	1.050	1.110
10	0.750	1.050	0.795	1.230	1.230	1.260
15	0.720	1.080	1.080	1.380	1.230	1.320
30	0.600	1.410	0.750	1.470	1.290	1.680
45	0.870	1.410	0.720	1.170	1.560	1.560
60	0.600	1.470	0.660	1.500	1.350	1.440
150	0.630	1.590	0.690	1.440	1.620	2.100
300	0.870	1.725	1.170	1.350	1.410	1.950

IRM #8618 Wax @ 120°C (cont'd)

Absorbance

Time(Min)	# 7	# 8	# 9	# 10	# 11	# 12
0	0.000	0.000	0.000	0.000	0.000	0.000
5	0.870	0.210	0.900	0.570	0.270	1.260
10	1.140	0.360	0.900	0.960	0.480	0.990
15	1.170	0.180	0.660	1.380	0.600	1.350
30	1.260	0.150	0.930	0.840	0.450	0.960
45	1.350	0.330	0.540	0.180	0.270	0.540
60	1.290	0.390	0.540	0.300	1.110	0.990
150	1.170	0.000	0.570	0.930	1.200	0.930
300	1.193	0.090	0.540	0.120	0.270	0.840

Table A-3 Raw data of the absorbance of titanium film colored product reacted in catechol/IRM Hewax wax solution.

IRM Hewax @ 130°C

Absorbance

Time(Min)	# 1	# 2	# 3
0	0.000	0.000	0.000
5	0.420	0.300	0.810
10	0.060	0.300	1.110
15	0.360	0.600	1.209
30	0.930	0.570	1.050
45	0.240	0.480	1.157
60	1.243	0.210	1.157
150	0.510	0.240	1.170
300	0.210	0.210	1.073

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