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PIGMENT COLOR RESEARCH REPORT

INSTRUMENTAL COLOR MONITORING OF MOLYBDATE ORANGE STRIKES

Period Covered

May 1976 - November 1976

FILE: 210.3

DATE: 11/17/76

KN-76-8

Issued - 11/17/76

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NEWARK PLANT

PIGMENT COLORS RESEARCH AND DEVELOPMENT REPORT

E. I. DU PONT DE NEMOURS AND COMPANY

TITLE - INSTRUMENTAL COLOR MONITORING OF MOLYBDATE ORANGE STRIKES

FINAL REPORT

Work Done by - A. R. Hanke

Report Written by - A. R. Hanke A R Hanke

Previous Related Reports - KN-76-7

Project Code - 4671-200

Period Covered - May 1976 - November 1976

Notebook Nos - E6153, E6158

ABSTRACT

Instrumental color measurement can be used to study the influence of various factors in the production of molybdate orange. The factors studied in this report are temperature, sodium chloride addition, Sb^{++} addition, effect of pH, effect of rate of addition of the CrO_4^{--}/MoO_4^{--} mixture, and the effect of a Pb^{++} excess.

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I. INTRODUCTION

This work was undertaken to show that instrumental color measurement can prove useful in monitoring the production of molybdate orange from the beginning of the strike to the final vat control. The basic idea of monitoring production of many pigments by on-the-spot instrumental color measurement is an obvious extension of this work.

II. PATENT SITUATION

No patent action is intended for any of this work.

III. SUMMARY AND CONCLUSIONS

A. The color monitoring technique involves placing a 2 liter beaker over the viewing port of the DU-COLOR meter. The quantities are adjusted so that the final volume is around 1 liter. An electric stirrer supplies sufficient vertical mixing to give reproducible and steady readings. The formations of a vortex that reaches the bottom of the beaker or the formation of air bubbles must be avoided.

From the DU-COLOR data, calculations are made of lightness, hue, and color intensity in U*V*W* color space. In most cases, it was the change in hue that was followed as various other factors were changed for a molybdate orange strike.

B. The following variables associated with molybdate orange production were studied using instrumental color measurement.

1. Effect of temperature during the strike and development of YE-698-D.
2. Effect of NaCl during strike and development of YE-698-D.
3. Effect of pH on molybdate orange with, and without silica/alum treatment.
4. Effect of amount of Sb^{+++} added during YE-698-D production.
5. Effect of rate of addition of the CrO_4^{--}/MoO_4^{--} solution.
6. Effect of Pb^{++} excess on the development step of YE-698-D.

C. The desired temperature during strike and development is around 65°F. At a temperature of 73°F, the color is noticeably yellower than at 65°F by an amount about equal to the shipping limit. This difference is apparent immediately after the strike and persists through all subsequent steps.

D. The addition of NaCl accomplishes two desirable effects. It causes the development of a redder product and it slows the subsequent degradation of molybdate orange.

E. For wide swings in pH, such as from 2.5 to 9.5, there is a reversible shift in hue with the high pH giving the redder hue. A permanent change due to pH is associated with the degradation of molybdate orange. At a pH of 3.5, after an induction period of around 100 minutes, there is rapid degradation of the silicate/alum treated molybdate orange slurry. At a pH of 6.0, the slurry is stable for at least two weeks and very likely, indefinitely. At a pH of 10 there is no severe degradation up to around a day but x-rays show evidence of the formation of some basic lead chromate.

F. The addition of Sb^{+++} causes yellowness and dullness. A plot of hue vs amount of Sb^{+++} shows a rapid change towards yellow in the range of zero to 1/2 the normal amount of Sb^{+++}. For increased amounts, the change is less rapid. The same holds true for color intensity. From the point of view of a subjective color change, there is a greater change in color intensity than in hue. The difference in hue between no Sb^{+++} and four times the normal amount is about that of a shipping limit unit. The difference in color intensity between no Sb^{+++} and the normal amount is about three times the shipping limit.

G. If the CrO_4^{--}/MoO_4^{--} mixture is dumped into the lead nitrate solution rather than added over a period of 18 minutes, the hue reaches a redder value and maintains this red advantage through all subsequent treatments. This holds for YE-698-D, YE-816-D, and YE-421-D type strikes. For YE-698-D type strikes, the difference amounts to around two shipping limit units. A possible explanation is that there is more molybdate orange degradation in the case of the 18 min. strike than for the dump strike because of longer exposure to a low pH in the case of the 18 min. strike.

H. A Pb^{++} excess has a marked effect in slowing the rate of formation of molybdate orange and the rate of degradation. The greater the Pb^{++} excess, the longer it takes to develop maximum redness. After reaching a red maximum, the greater the lead excess the longer it takes to degrade back to yellow. In the range of 2.5% to 8% Pb^{++} excess the maximum redness is about the same and is greater than that reached for smaller or larger Pb^{++} excesses. At a Pb^{++} excess of 0.5%, the red maximum is considerably yellower than at 2.5% Pb^{++} excess, it is more detrimental to let the Pb^{++} excess get in the rnage of 0.5% than in the range of 21% Pb^{++} excess.

These observations relate to the mechanism of molybdate orange formation and degradation. The intial precipitate of rhombic $PbCrO_4$ and tetragonal solid solution converts to molybdate orange but there is also degradation of the molybdate orange crystal. The rate of degradation becomes so great as the Pb^{++} excess approaches zero that very little molybdate orange remains.

IV. EXPERIMENTAL DETAILS AND DISCUSSION

This section is a compilation of monthly summaries dealing with the application of instrumental color measurement to molybdate orange formation and degradation. The summaries contain notebook references where one can obtain further experimental details. The summaries have been edited to correct some typographical errors and show some re-calculated values for Pb^{++} excess including an estimate for sulfate in the chrome liquor.

INSTRUMENTAL COLOR MEASUREMENT AS A TOOL IN MOLYBDATE ORANGE PROCESS CONTROL ARH
71-200 NB E6153-17

It has been shown previously (KN-75-2) that instrumental color measurement on the final vat control of molybdate oranges is useful in predicting the tinctorial properties of the dry color. The attempt is now being made to monitor the slurry color from the beginning to the end of a molybdate orange strike. This is being accomplished by carrying out a strike in a beaker on the DU-COLOR allowing continuous color monitoring through the bottom of the beaker. A trial YE-698-D strike was carried out with no serious technical difficulties.

Work will continue in the attempt to show that some characteristic of the color changing profile can provide a useful monitor for moly orange production.

INSTRUMENTAL COLOR MEASUREMENT FOR MOLYBDATE ORANGE PROCESS CONTROL

71-900 NB E6153-15,
E6158-1,2 ARH

Instrumental color measurements are being made on laboratory strikes of YE-698-D molybdate orange. The color is being monitored by carrying out the complete strike in a beaker placed over the viewing port of the DU-COLOR meter. Figure 1 shows the change in hue with time for strikes run at 65°F and 73°F. The hue is calculated as an angle in U*V*W* color space. The vertical regions on the plot signify hue readings immediately before and after the addition of the indicated ingredient.

It can be seen that the DU-COLOR is sensitive enough to pick up the almost immediate color changes that occur when the various ingredients are added. The abrupt change to redness when soda ash is added is related to the pH change from the acid to the alkaline side. Other abrupt color changes are undoubtedly related to the precipitation of hydrous silica, alumina, and the reducing action of the trivalent antimony solution. Another point to be observed is that the 73° strike is yellower, prior to the first addition of soda ash, than the 65° strike. This yellowness persists throughout the strike and is due to the higher temperature. A strike run at 80°F, not shown in the figure, shows a bend in the curve at a higher hue value (yellower) than the 73°F curve. This means that at a point during development, even before the addition of the first soda ash, it will be possible to tell that the final product will be substandard. Unfortunately, there is

nothing one can do to "save" such a strike but it may be possible to establish the cause for the failure to develop sufficient redness and correct it for the following strike.

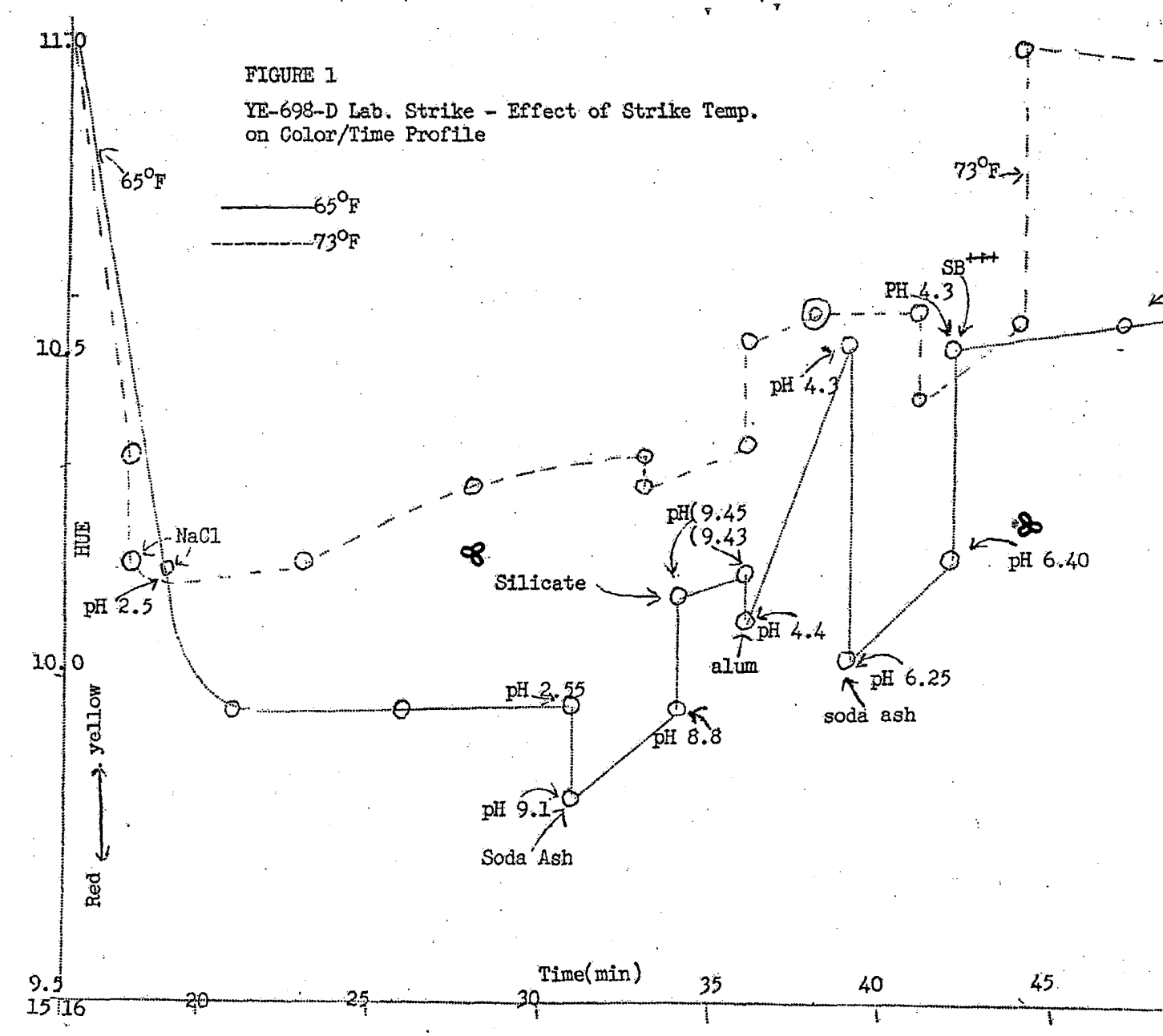
These experiments show that color measurements during a strike can be rapidly obtained and can give early warning of trouble. Color monitoring could also be used as part of the strike procedure. For example, instead of using a pre-set time during development before adding the other reagents, begin adding them at the time of maximum redness.

An inspection of the curves shows a general slope to yellowness after the point of maximum redness is reached. This suggests a slow deterioration of the molybdate orange crystal while in the mother liquor and indeed, without the silicate treatment, overnight standing shows considerable loss of redness. This suggests that subsequent addition of the reagents after development should not be delayed.

Observing the color profiles of other strikes while modifying some parameter will undoubtedly give rise to other thoughts that could aid in quality control. Work along this line will be continued. This will include the actual monitoring of plant strikes.

FIGURE 1

YE-698-D Lab. Strike - Effect of Strike Temp. on Color/Time Profile



INSTRUMENTAL COLOR MEASUREMENT OF MOLYBDATE ORANGE STRIKES

E6153-17. E6158-1 thru 7 ARH

Plant and laboratory strikes of YE-698-D and YE-421-D have been color monitored with the intent of learning what the color readings should be during a strike that will result in a product close to the standard. Such information is now available for YE-698-D and YE-421-D.

In addition to monitoring slurry color for quality control, inprocess color measurement can serve as a tool to study the effect of variables on molybdate orange formation. Such measurements have the considerable advantage of being made almost immediately and hence are not influenced by inadvertent variable treatment given later. For example, if one is studying the influence of a variable early in a strike and it is being followed by the color of the final dried pigment, this final color will also be influenced by all subsequent treatments such as pigment

surface treatments, grinding, and drying conditions. An on-the-spot color measurement of the slurry circumvents all this. Furthermore, color measurement is one of the most sensitive measuring tools that we possess. It is often more sensitive to changes in the physical and chemical makeup of a pigment than other tools such as X-ray diffraction and electron microscopy.

Following are some examples of how "inprocess" color measurement can serve as a tool to study molybdate orange formation and hopefully optimize certain tinctorial properties.

A. Effect of NaCl on Molybdate Orange Formation E6153-17

A YE-698-D type strike was run with the NaCl added at the customary time during the strike. None of the following customary additions were made and the color changes were followed with the DU-COLOR.

Another strike was run but no NaCl was added. Figure 1 shows the plot of hue in U* V* W* color space with time. It can be seen that the NaCl accomplishes two things, both desirable. First, with NaCl the slurry becomes redder than without NaCl before it turns around and becomes yellower again. Second, with NaCl the rate of increase in yellowness after the turn around is far less than without NaCl. The presence of NaCl allows a redder product and also acts to inhibit the degradation of the molybdate orange crystal.

B. Influence of pH on Slurry Color

1. Zigzag Change in pH E6158-1

A YE-698-D strike was carried out. At the time where soda ash would normally be added, caustic was used instead, to adjust the pH to 9. Periodically thereafter, the pH was shifted in zigzag fashion from around 9 to 2.5 using caustic and nitric acid. Figure 2 shows a plot of the hue in U*V*W* color space.

It can be seen that the pH change over this range appears to have a reversible effect on the color. This reversible effect is riding on an irreversible color change towards yellow which undoubtedly relates to the degradation of the molybdate orange crystal.

2. Effect on Molybdate Orange Slurry of Stepwise pH Change E6158-6

A YE-698-D strike was carried out that included the addition of silicate and plant alum but did not include the addition of Sb^{+++}. After the second addition of soda ash the pH was adjusted to 9 with caustic and then changed in step fashion from 9 to 2.5 and back to 9 using nitric acid and caustic. There was a 1 to 3 minutes interval between each step.

Figure 3 shows a plot of hue in U*V*W* color space vs time with indicated pH at each time. It is seen that there is very little change in hue as the pH is dropped from 9 to 3 but in the vicinity of pH 3 there is a sharp turn to yellow. This shift to yellow continues even when the pH is reversed and moved back up. When the pH reaches the region of 7, the rate of yellowing decreases but by now the molybdate orange has been severely degraded.

This experiment serves to illustrate how color measurement on slurries can indicate the degree of stability of molybdate orange as a function of pH. This experiment suggests that even with a silica/slum treatment, discernible degradation of molybdate orange can take place in a few minutes at a pH of around 4 to 3. A repeat experiment giving more attention to the pH range 5 to 3 with time intervals greater than three minutes will allow a more precise measure of the influence of pH on molybdate orange stability.

C. Influence of Amount of Sb^{+++} on Color E6158-7

A YE-698-D strike was carried out but when it came time to add the Sb^{+++}, the pH was adjusted to 6.5 with HNO_3 and only ½ the normal amount of Sb^{+++} was added. After again adjusting to pH 6.5 with caustic, another ½ portion was added. This was continued with time intervals around two minutes to give a ladder series of total Sb^{+++} of 0, 1/2, 1, 1½, 2, 3, 4 times the customary amount. The pH adjustments to 6.5 were made to prevent any reversible pH effect on hue from influencing the results.

Figure 4 shows a plot of hue and color intensity vs amount of Sb^{+++} expressed as a fraction of the customary amount. It is seen that the hue changes towards yellow quite steeply in the range of zero to ½ the normal amount of Sb^{+++}. From then on, the change is less rapid but the trend toward yellowness continues almost linearly up to at least four times the normal amount of Sb+++. The color intensity also falls off quite steeply in the low Sb+++range and then falls off to a lesser extent as the Sb+++ increases.

These changes can be considered in terms of visual color differences by realizing that an instrumental hue difference of around 0.33 represents the shipping limit for visual hue and an instrumental color intensity difference of around 1.4 represents the shipping limit for the visual intense/dull color reading. From this point of view the hue difference between no Sb+++ and four times the normal amount of Sb+++ will be about that of the shipping limit. This is not the case with color intensity, however. Here the difference between no Sb+++ and the normal amount is about three times the shipping limit. This means that the Sb+++ has a greater visual effect on color intensity than on hue. The curves also show that the normal amount of Sb+++ is well chosen to lie in the region where a variation in the amount added, will have the least tinctorial effect.

D. Influence of Rate of Addition of CrO_4^{--}/MO_4^{--} on Molybdate Orange Color E6158-2,3

Two YE-698-D strikes were carried out. For one, the time of addition of the CrO_4^{--}/MO_4^{--} solution was the normal 18 minutes and for the other, the solution was dumped in. In each case the NaCl was added immediately after the addition of the CrO_4^{--}/MO_4^{--} solution. In the case of the dump strike, the first soda ash was added near the time of reddest hue.

Figure 5 shows the HUE/TIME profile for both strikes. For both strikes, the hue reaches its reddest point at about the same time (around 32 minutes) but the dump strike slurry is redder than the 18 minute strike. This hue advantage is maintained throughout all the subsequent additions of the usual reagents. The two products finish with a hue difference that would exceed shipping limits. The difference in hue cannot be attributed to the fact that for the dump strike, the

first soda ash was added at the point of maximum redness because the slurry was redder than the 18 minute strike even before the addition of the first soda ash. A possible explanation is more Molybdate Orange degradation in the case of the 18 minute strike than for the dump strike because of longer exposure to a low pH in the case of the 18 minute strike.

Work is continuing to more rigidly define the conditions for molybdate orange formation and degradation using inprocess color measurements.

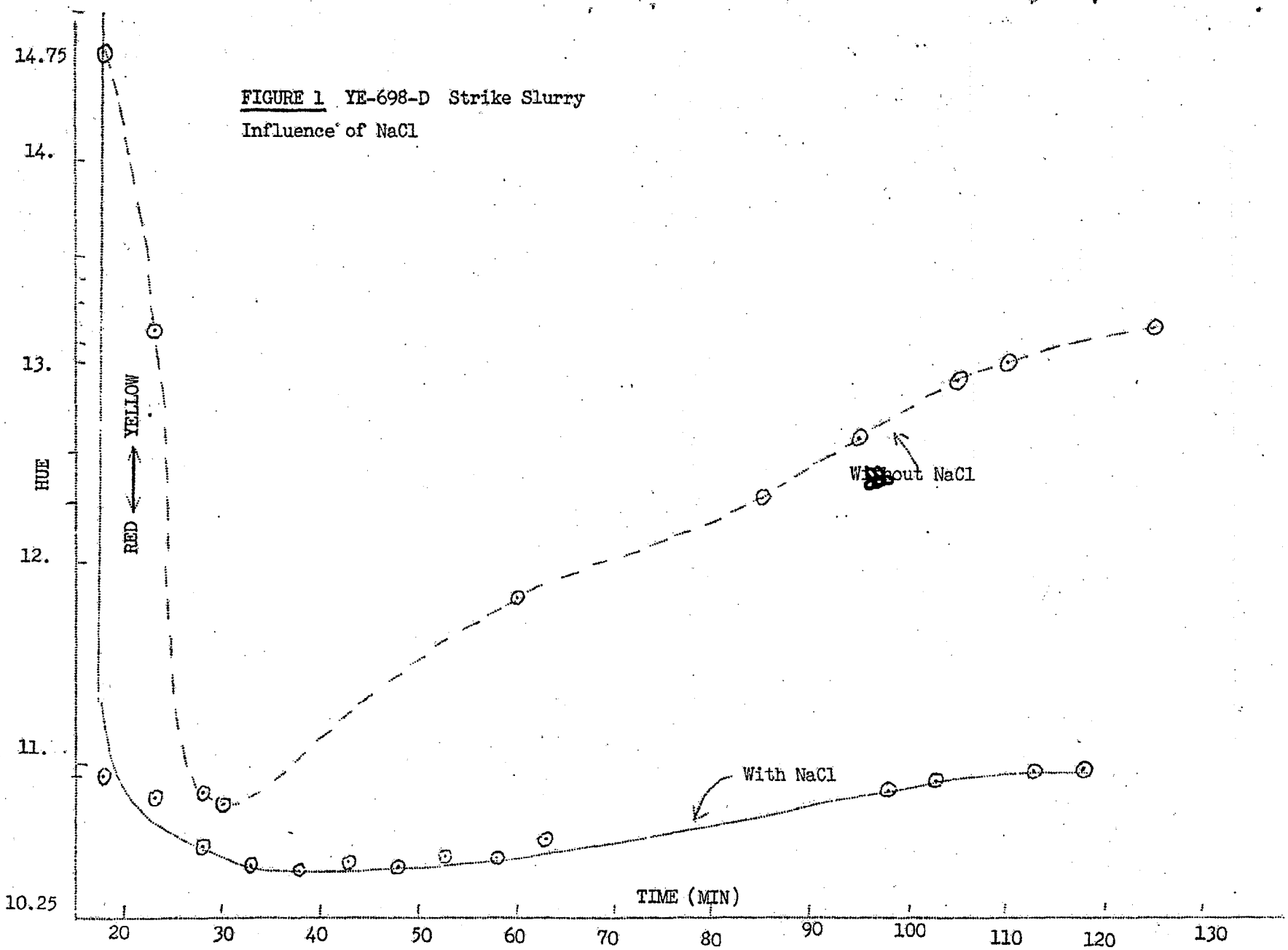


FIGURE 1 YE-698-D Strike Slurry
Influence of NaCl

FIGURE 2

YE-698-D Strike Slurry

Influence of pH on Hue.
Illustrated reversible Hue change.

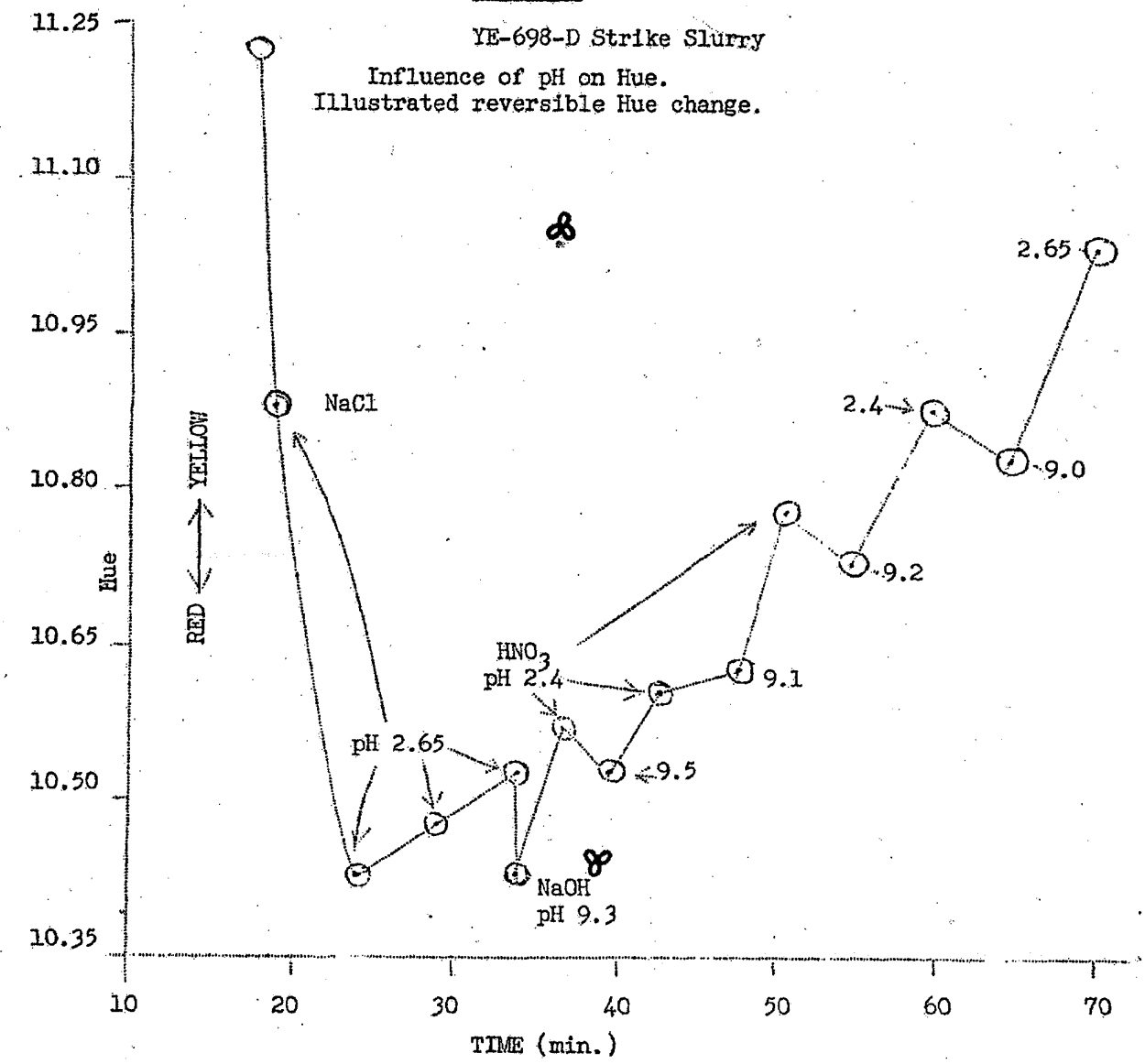


FIGURE 3

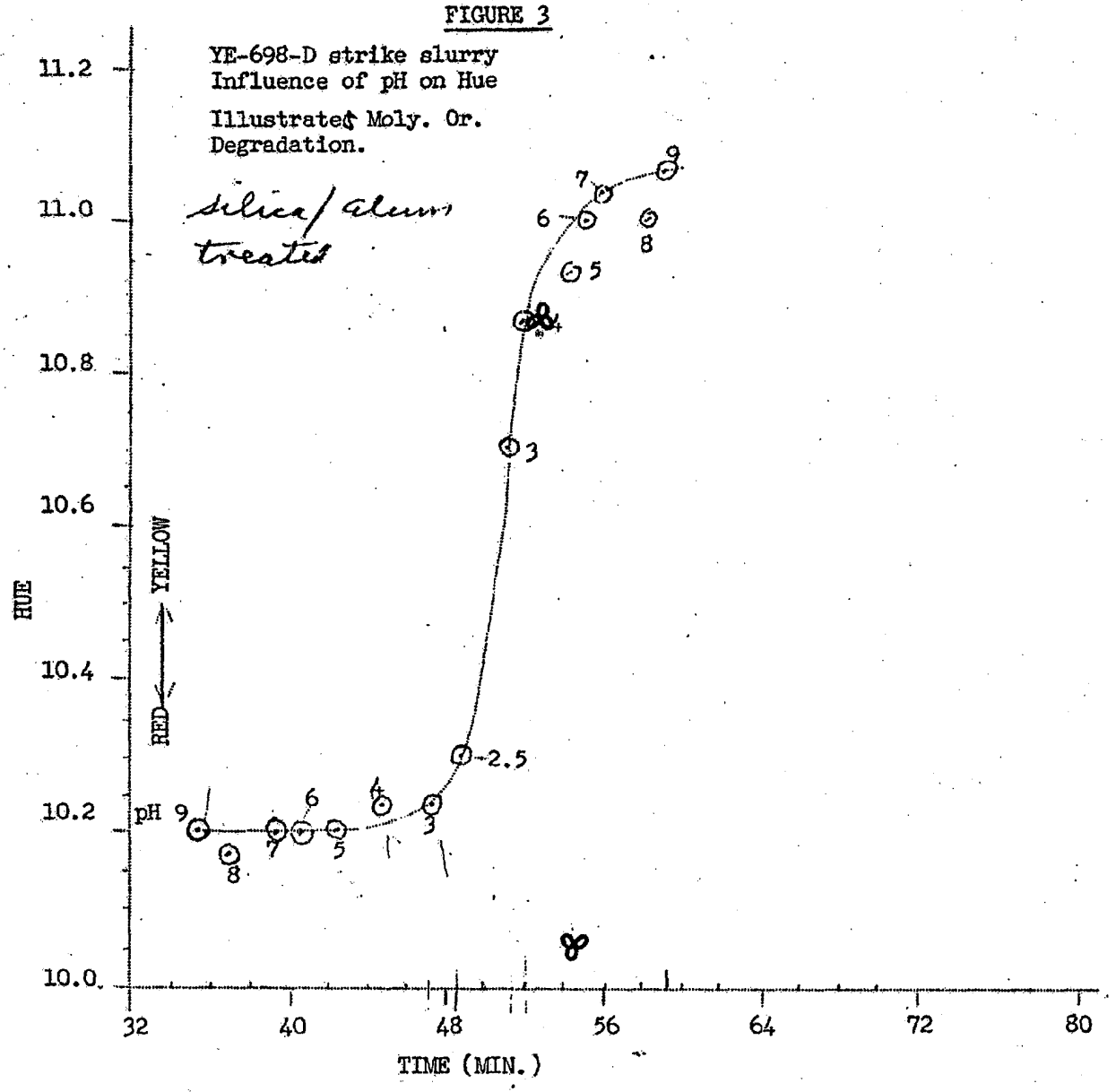


FIGURE 4

YE-698-D Strike Slurry
Influence of Sb^{+++}

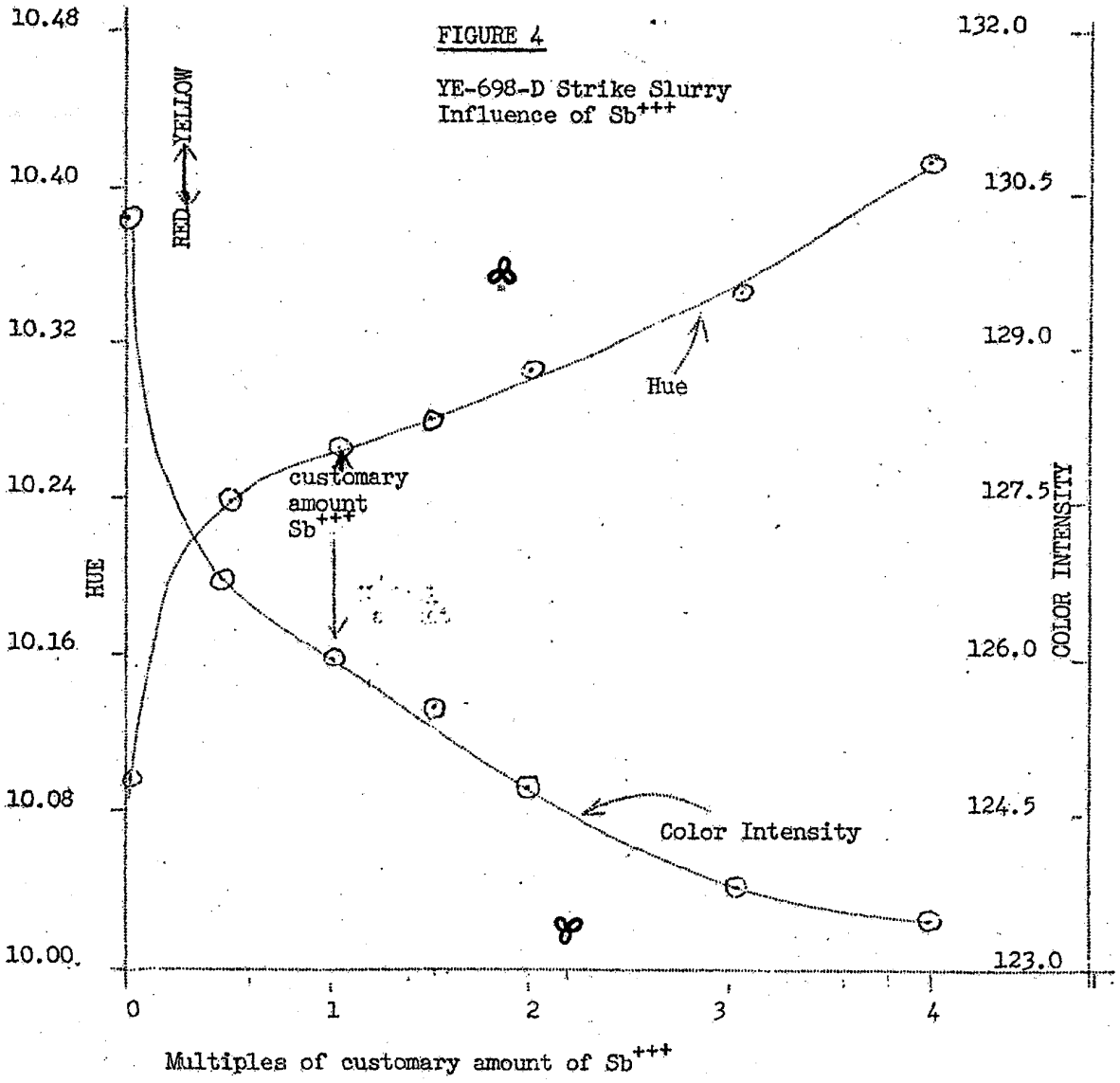
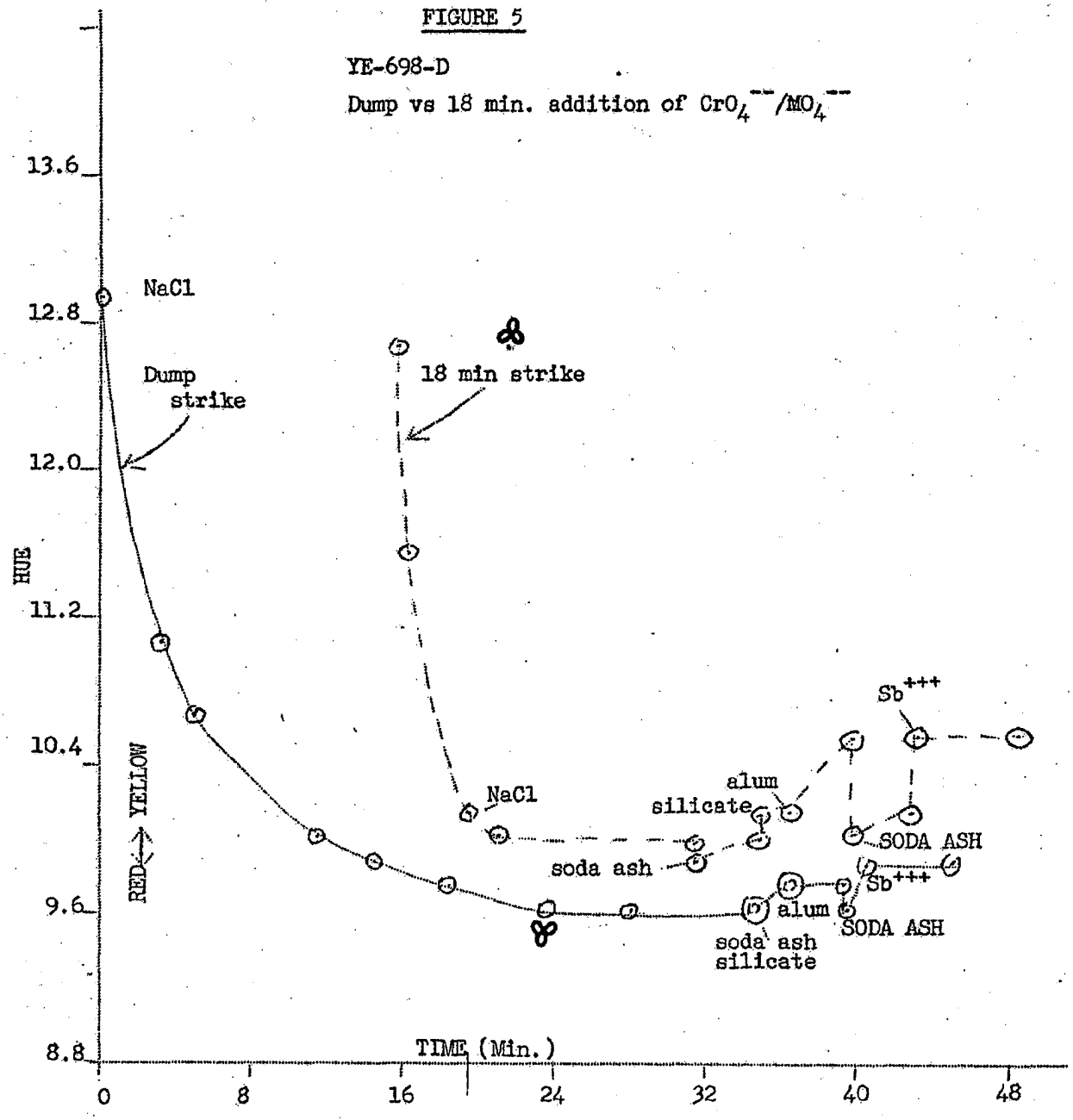


FIGURE 5

YE-698-D

Dump vs 18 min. addition of CrO_4^{--}/MO_4^{--}



B. Rate of Molybdate Orange Degradation as Function of pH E6158-11 ARH

Laboratory YE-698-D type strikes were carried out that included the addition of silicate and alum but the Sb^{+++} was omitted. At the point in the strike where the second soda ash is normally added, the pH was adjusted to a pre-selected value using nitric acid or caustic. Stirring was continued and the color monitored with the DU-COLOR. The selected pH's were 3, 3.5, 4.0, 4.5, 10.

Figure 1 shows the HUE/TIME profiles for the various pH's. There is some evidence that at a lower pH there is an induction period where the change is slight and after this period there is rapid degradation. This could relate to the time required to strip off the protective coating and this could constitute a test for the effectiveness of the coating. It is also of interest to note that the curve at pH 4.5 is much the same as that of pH 10. The degradation is slight but unmistakable over around 300 minutes but over a much longer period of time the molybdate orange severely degrades at a pH of 4.5 but does not at a pH of ~~11~~ 10. It is already well established that at a pH of around 6.5, coated molybdate orange slurries are stable practically indefinitely. The fact that even coated molybdate orange is unstable at a pH of 4.5 can be of some concern, if in its end use it will be subjected to a pH 4.5 environment for a long time.

C. Rate of Molybdate Orange Degradation as Function of Lead Excess

E 6158-12 ARH

YE-698-D type strikes were carried out in the laboratory but the CrO_4^{--}/MoO_4^{--} solution was dumped into the $Pb(NO_3)_2$ solution rather than added over a set period of time. After addition, the pH was adjusted to 2.3 which is close to the pH expected at that point in the strike. None of the subsequent reagents was added. The color change with time was monitored with the DU-COLOR. The only variable between strikes was the amount of CrO_4^{--} solution added. For each strike a different amount of CrO_4^{--}/MoO_4^{--} solution was added creating a ladder series with different amounts of Pb^{++} excess. The excess was calculated as a per cent in

NOTE The corrected figures include the sulfate present in the chrome liquor.

excess of the stoichimetric amount based on the reaction with $CrO_4^=$, $MoO_4^=$, and ~~added~~ $SO_4^=$. ~~The amount of $SO_4^=$ originally in the chrome liquor was ignored. This means that the actual Pb^{++} excess is a little less than the calculated value because there is actually a little more $SO_4^=$ in the $CrO_4^=/MoO_4^=$ solution than that used in the calculation.~~

2.5% 7.9% 20.6% - 13.9%

Figure 2 shows the HUE/TIME profile for the various Pb^{++} excesses. It can be seen that the amount of Pb^{++} excess has a profound effect on the rate of molybdate orange degradation. At ~~10.5%~~ Pb^{++} excess, the rate of degradation is far less than that at ~~4.7%~~ Pb^{++} excess. In the region of ~~23.5% - 16.6%~~, the rate of degradation is reduced still further. But note that the development time to reach maximum redness becomes longer as the Pb^{++} excess increases. Also at higher Pb++ excesses, the slurry does not reach as red a point as at lower Pb++ excesses. In the range ~~4.7% - 10.5%~~ the slurry reaches about the same degree of redness but at higher percentage this degree of redness is never reached even with an extended time.

2.5% - 7.9% 2.5% - 8% 8%

These data suggest that, although a Pb++ excess slows degradation, which is desirable, it does not allow as full a development of redness as that which occurs at a lower Pb++ excess and this is undesirable. The data also suggest that in the range of ~~5% - 10.5%~~ there is very little change in maximum redness but a large change in the rate of degradation. This means that if the Pb++ excess is not allowed to get much above ~~10%~~, there will be very little sacrifice in redness but some advantage in increased stability. Another observation relates to the question, "How long can an uncoated molybdate orange be exposed to a pH of 2.5 before there is a discernible change in hue?". A reasonable detectable limit on the hue scale is around 0.1. The ~~4.7%~~ Pb++ excess curve shows a rate of degradation such that in about three minutes there would be a discernible change in hue. This points up the importance of not allowing the molybdate orange to be exposed to the development pH of around 2.3 with a low Pb++ excess for a length of time exceeding three minutes. Recall, however, that it was shown previously that the addition of NaCl slows degradation and does not impair the development of redness. The addition of NaCl can, therefore, be considered as a safeguard against excessive degradation.

2.5%

This experiment serves as an excellent example of the use of instrumental color measurements. In this experiment the molybdate orange is unstable and at times is changing rapidly. It would have to be isolated, dried, a rubout made and measured under conditions that would allow very little degradation. These are rather difficult technical requirements. Getting immediate color measurements on the slurry completely eliminates these difficulties.

We will continue to aid Manufacturing in applying instrumental color measurement to "in-process" control.

BISMUTH VANADATE YB-200-D NB 6154 JFH

Bismuth Vanadate, formerly PGL-20, is now coded YB-200-D. Appropriate SF numbers for intermediate stages have also been assigned.

The second four pound sample prepared was sent to F&F Troy, Michigan who reported the acid resistance as unacceptable.

A decision was made to proceed with a Semi-Works run from Semi-Works oxide-coated base. Thirty-five pounds (SW 76-00811) was prepared. The quality by the

FIGURE 1

Rate of Degradation as Function of pH

Silica/Alum Coated YE-698-D

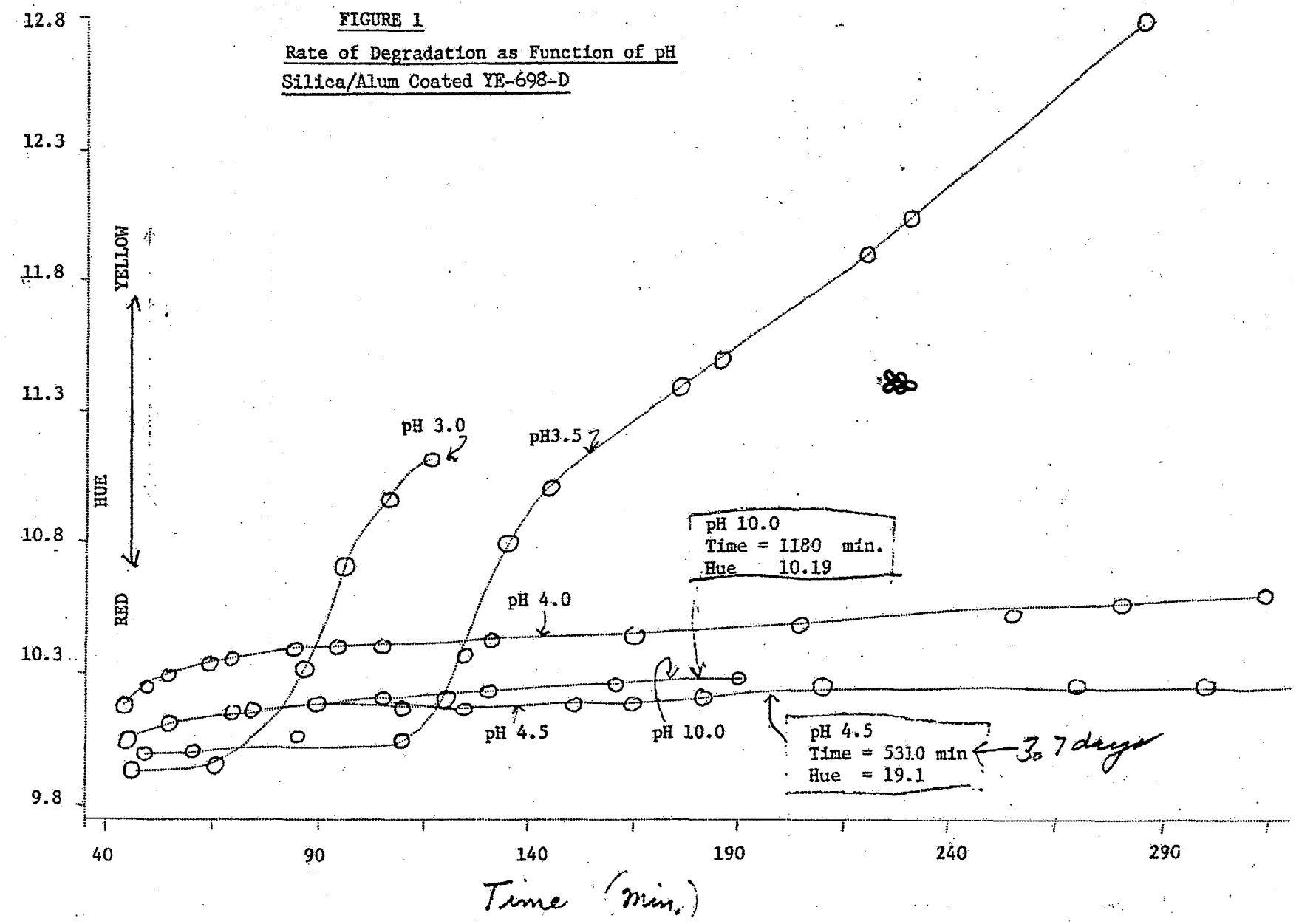
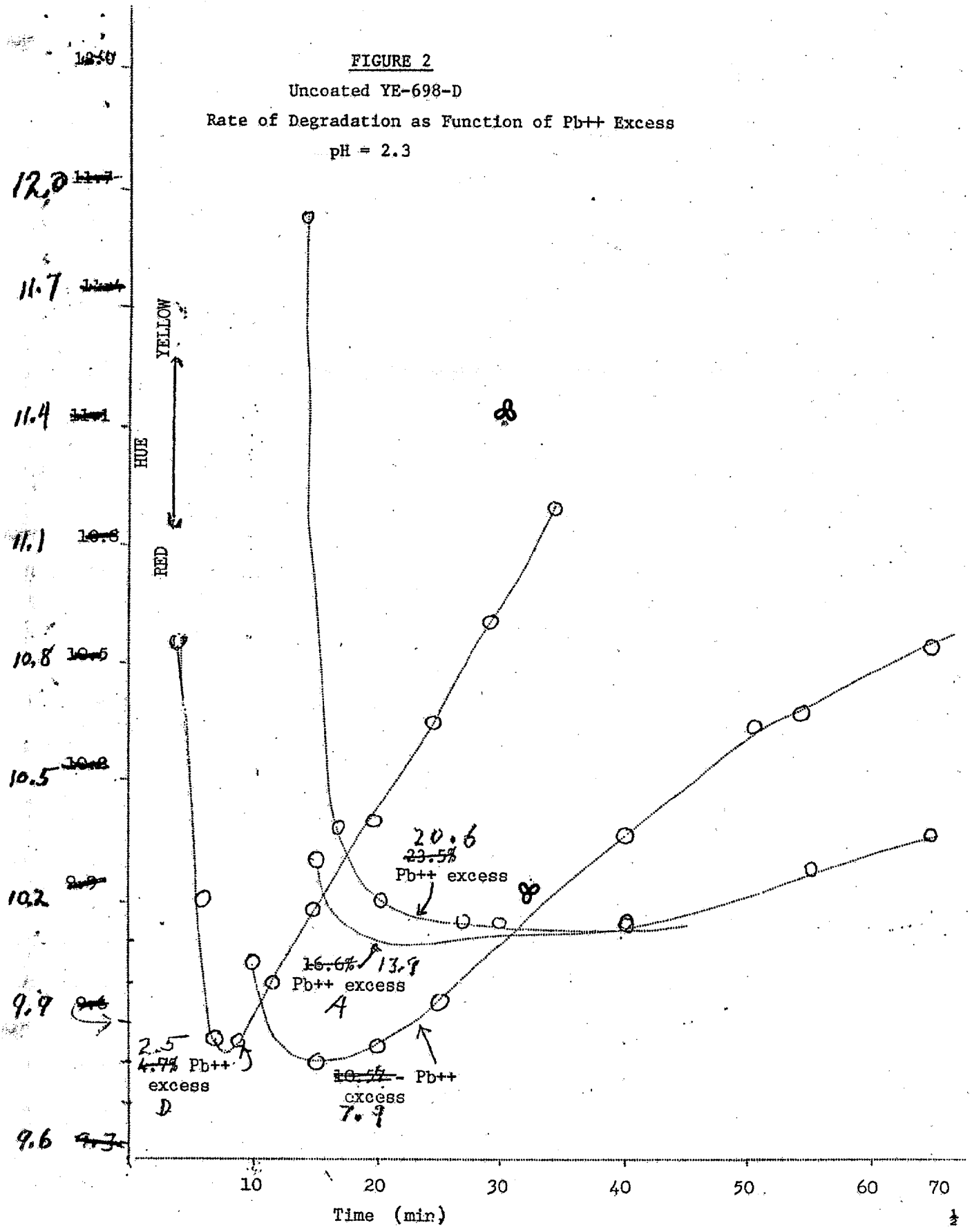


FIGURE 2

Uncoated YE-698-D

Rate of Degradation as Function of Pb++ Excess

pH = 2.3



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INSTRUMENTAL COLOR MEASUREMENTS OF MOLYBDATE ORANGE STRIKES ARH

A. Rate of Molybdate Orange Degradation as Function of pH E6158-11

In the previous summary an experiment was described in which a series of YE-698-D type slurries, exclusive of Sb^{+++}, was allowed to stir at pre-selected pH values. The slurry, pre-set at pH 4.5, showed severe degradation within 3.7 days. Continuing experiments show that at a pH of 5.0 and 5.5 there is severe degradation within four days. At a pH of 6.0 the slurry did not degrade even after a week. This means that final vat controls adjusted to a pH no lower than 6 can be considered stable for at least a week and very likely longer.

It is of interest to note that at a pH of 10.0, there is no severe tinctorial degradation up to 0.8 days, but an x-ray record shows evidence of a small amount of basic lead chromate of the YO-34-D type. No further work is planned for this experiment.

B. Rate of Molybdate Orange Degradation as a Function of Lead Excess

E6158-12 ARH

In the previous summary it was shown that the formation and degradation of molybdate orange was slowed considerably as the Pb^{++} excess increased. Furthermore, increased redness was observed at the lower Pb^{++} excesses with the redness about the same in the region of ~~4.5% to 18.5%~~ Pb^{++} excess. All of the strikes in this ladder series were dump strikes.

The experiment has been extended to still lower Pb^{++} excesses, namely ~~3%~~ and ~~2%~~. Figure 1 shows the change in hue with time. It also includes the curves for ~~4.7%~~ and ~~16.6%~~ Pb^{++} excess from the previous experiments for comparison purposes. It can be seen that at the ~~3%~~ Pb^{++} excess level, less redness is developed and the rate of degradation is greater than at ~~4.7%~~ Pb^{++} excess. At the ~~2%~~ Pb^{++} excess level, a maximum redness was not caught by the DU-COLOR. It probably exists but is too transient to be easily observed. At any rate, it would be at a point far yellower than the maximum redness at ~~4.7%~~ Pb^{++} excess. Notice, too, that at ~~2%~~ Pb^{++} excess, molybdate orange is degrading at the most rapid rate of all and the reddest point is already far yellower than the reddest point of the ~~16.6%~~ Pb^{++} excess curve. Too great a Pb^{++} excess and too small a Pb^{++} excess both contribute to yellowness but the effect is most pronounced at a low Pb^{++} excess.

This can be explained by realizing that after the initial precipitation of rhombic $PbCrO_4$ and tetragonal solid solution, molybdate orange is both being formed and degraded. The rate of degradation increases so rapidly with decrease in Pb^{++} excess that at the ~~2%~~ level it is so large that no acceptable amount of molybdate orange is ever produced.

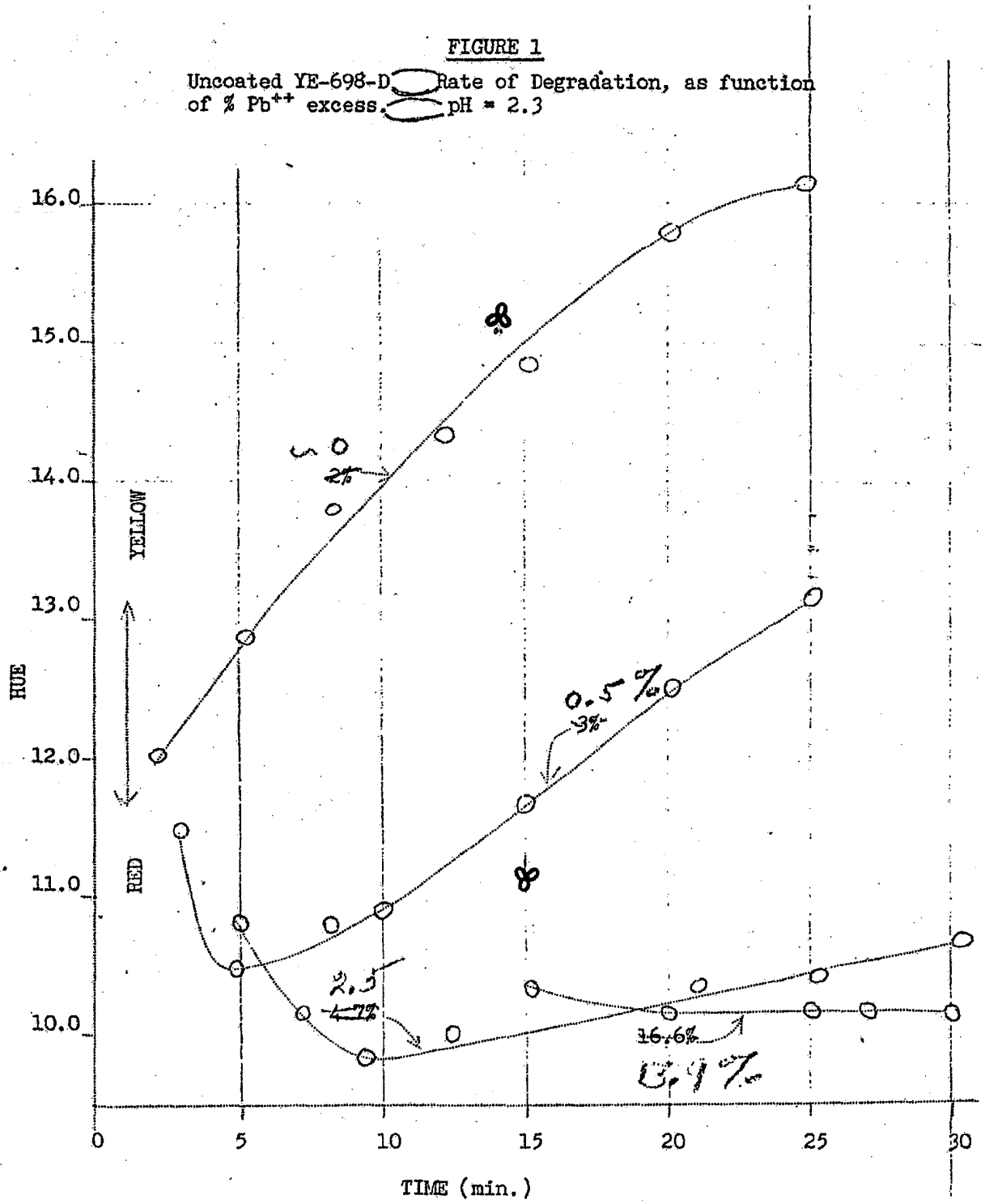
This means that for a dump strike, it is necessary to have a higher Pb^{++} excess than for a strike where the chrome molybdate solution is added over a period of time. It also suggests that with a higher Pb^{++} excess, the addition of NaCl becomes less critical because the increased Pb^{++} excess will impart some stability making it less imperative to rapidly invoke the stabilizing action of the NaCl. No further work is planned for this experiment.

BHP:mnm

atc.

FIGURE 1

Uncoated YE-698-D ○ Rate of Degradation, as function of % Pb^{++} excess. ⌒ pH = 2.3



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11. I. H. Dunn, Pigm., Newark
12. T. R. Becker, Pigm., Newark
13. E. J. Mead/C.H.Muendel, Pigm., Exp. Station
14. Newark Numerical File - 210.3
15. Newark LIbrary - Central Report Index
16. Newark Library - Central Report Index
17. Extra
18. Extra
19. Extra

107-129 missing!