# Developing improvement technology in pre-etching process for the Shadow Mask quality of flat color TV

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#### **Abstract**

Recently CRT is getting flatted, As change of CRT trend from normal type to Flat type, the material of Shadow Mask was also changed from AK(Aluminum Killed) to Invar(Fe-Ni alloy) materials

Until now we have used just AK(Aluminum Killed) for normal type TV(not flat type), but main raw material of shadow mask component was changed.

. However recently Invar(Fe-Ni alloy) materials, which has advantage of Low Thermal Expansion and High Strength, has been developed as well as applying in mass production as CRT's trend has become more flat and fine pitch.

As main raw material of shadow mask component was changed, conditions of process were changed. One of them, the importance of pre-etching process (assistant process for developing & etching) is improved because there are so many particles in the pre-etching bath because of Ni compounds.

Since the solubility of Ni in pre-etching solvent is very low related to Fe's, so the compounds of Ni happen to make particles.(the solubility of Fe is twenty times Ni's) that particles happen to make process troubles and NG productions so to clear the particles we had to established high cost filtering system, but it is useless.

As time goes by the quantity of particles (Ni compounds) was increased because of the capability of filtering system was not enough, the particles was produced continuous in bath, and it make quality problems.

Hence we tried to develop the new pre-etching solution to remove the particles (Ni compounds) and to cost down the filtering system's running cost. But in improving the solution we discovered the new pre-etching solution made the PR developing better.

In former solution there were three kinds of chemistry (COOH)2, H2O2, H2SO4 first the function of (COOH)2 is drilling the surface of Invar, during this mechanism Ni compounds occurred. Second the function of H2O2 is removing the PR fringe (half UV exposure zone on PR(PVA)), Third the function of H2SO4 is the catalysis of (COOH)2

In those, (COOH)2 was the main reason to make the Ni compounds. So to improve the solutions we had to change (COOH)2 to the other material. the chemistry we improved was a complex chemistry based on H2SO4. after using this chemistry the particles problem was disappeared and there was another advantage cut down the PR fringe.

The New solution made the function of H2O2 better so the PR developing improved. To be direct the catalyst of the new solution helped the H2O2. anyway First thing after change the solution the quality of shadow Mask for flat color TV was improved & the yield also improved.

But the more important thing is how to control the new solution. So we accepted the new concept which was the degree of freshness. The degree of freshness is based on non-reacted solution which was 100% (the degree of freshness) and calculated the melted Ni quantity as time goes by. So we made the gauging liner plot.

In conclusion, many companies tried to make fine pitched Shadow Mask ,generally to make quality jump up it needed a lot of cost & persons .in this case the shift of core material made it possible.

## 1. Introduction

Shadow Mask is a thin metal sheet with hundreds of thousands of small holes on it. It is placed behind a monitor screen inside the CRT. Shadow Mask, determining the distinction of images on the monitor screen, is one of the three key components of Color

Braun tube. Until recently, Shadow Masks were made from AK(Aluminum-killed) steel possessing superior formability and etching ability and Invar steel possessing low thermal expansion coefficient faction of 10 times compared to AK.

Recently CRT is getting large-sized, flatness and high fine pitched in the meantime the raw material for Shadow Mask is in rapid progress of thin, low thermal expansion and high strength.

There are two different types of Shadow Mask such as Tension and Formed Type applied to CRT Flatness. The main material applied to tension type is mostly AK(Aluminum-Killed) and formed type is mainly Fe-36%Ni Invar alloy.

The surface of AK (or Fe-36%Ni Invar alloy) which is exposed after developing process is covered with thin PR(Photo Resist) and passivation layer, this thin PR(Photo Resist) and passivation layer interrupt the uniform process in the first stage of the etching process. This situation influence the fine hole making, Before etching, For the uniform etching We have to remove the rest PR(Photo Resist) and passivation layer with chemistry by chemical grinding.

In AK, There is no problem. Recently. As Invaralloy's quantity increase, The problems start to happen

Therefore, to solve the problems, We are going to find out most appropriate chemistry through chemical composition

## 2. The result of Analysis

## 1. 1st Problem: Particles

As we used the Invar , there are so many particles in the pre-etching process. We checked the particles of the chemistry in the AK pre-etching bath. Most of particles distributed 2  $\mu\text{m}\sim5\mu\text{m}(\text{fig 1})$  and as time goes by just the quantity of particles were increased but the size of particles were not increase, those size of particles is not influenced the quality of the Shadow Mask. So there were not particles problem in AK.

However recently Invar(Fe-Ni alloy) materials we used in that case particle problem happened. From the result of chemistry in the Invar pre-etching bath most of particles size are over than  $5\mu$ m and the size is increase because there are increasing seeds.

The result of seed analysis is like that.

The main material of the pre-etching chemistry is oxalic acid ((COOH)2), it reacts with Ni and make seeds. The solubility of the nickel hydroxide is 8~10mg/liter in pre-etching chemistry. From this result the quantity of nickel hydroxide is 2.5kg/day(it is very difficult to control this quantity of nickel hydroxide by filtering system). But the solubility of ferric hydroxide is 180mg/liter, so there is no seeds to make problems.

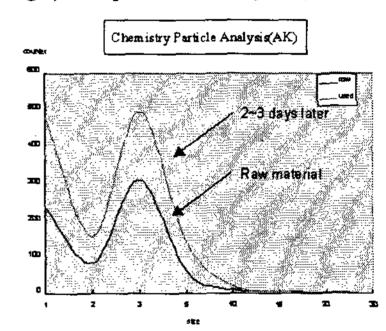
Therefore it needs change the pre-etching chemistry make no seeds but it have to do same role in pre-etching bath.

Table1) The quantity of nickel hydroxide

(1 line  $0.5\mu m$  etching)

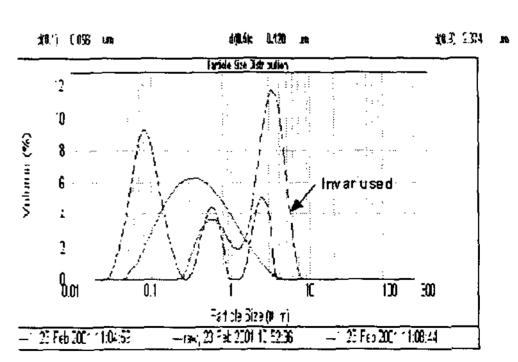
수산니켈 2수화물 용출양=	1.757	g/min
수산니켈 2수화물 용출양=	105	g/hr
수산니켈 2수화물 용출양=	2,530	9/일
수산니켈 2수화물 용출양-	75,898	9/월

Fig1) the particle analysis(AK)



(분석기:Hiac/Royco 800A)

Fig2) the particle analysis(Invar)



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The new pre-etching chemistry's mechanism is

$$Fe + H_2SO_4 \rightarrow Fe^{+2} + 2e^{-} + 2H^{+} + SO_4^{2-}$$
 $cat.$ 
 $H_2O_2 + 2H^{+} + 2e^{-} \rightarrow 2H_2O$ 

therefore

$$Fe + H_2SO_4 + H_2O_2 \rightarrow FeSO_4 + 2H_2O$$

and

$$Ni + H_2SO_4 \rightarrow Ni^{+2} + 2e^- + 2H^+ + SO_4^2$$

$$\cot$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
  
therefore

$$Ni(s) + H_2SO_4 + H_2O_2 \rightarrow NiSO_4 + 2H_2O$$

After change the chemistry, there is no particle problem and filtering system so both quality and cost was better than former system.

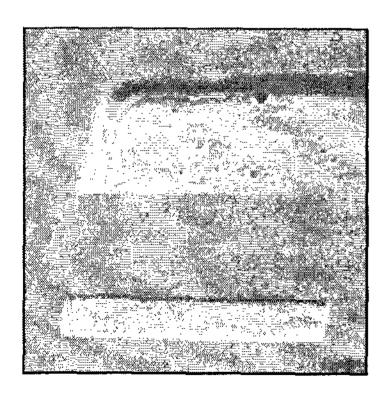
2. 2<sup>nd</sup> Problem: Sharpness after developing

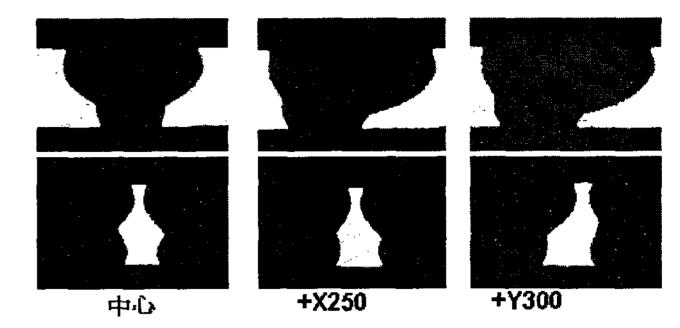
CRT is getting large-sized, flatness and high fine pitched in the meantime, but the PR is same. to change the PR & PR suffering system, it needs much money & long time. The appearance of developing hole is very rough(fig 3) to make the high fine pitched Shadow Mask.

To gain high grade quality(fine-pitched shadow mask) we have to improve the sharpness of PR after developing.

The main reason of poor sharpness is the function of H2O2 is weak to melt the fringe PR after developing process.

fig3) The appearance of developing hole(SEM) (after treat of H2O2)

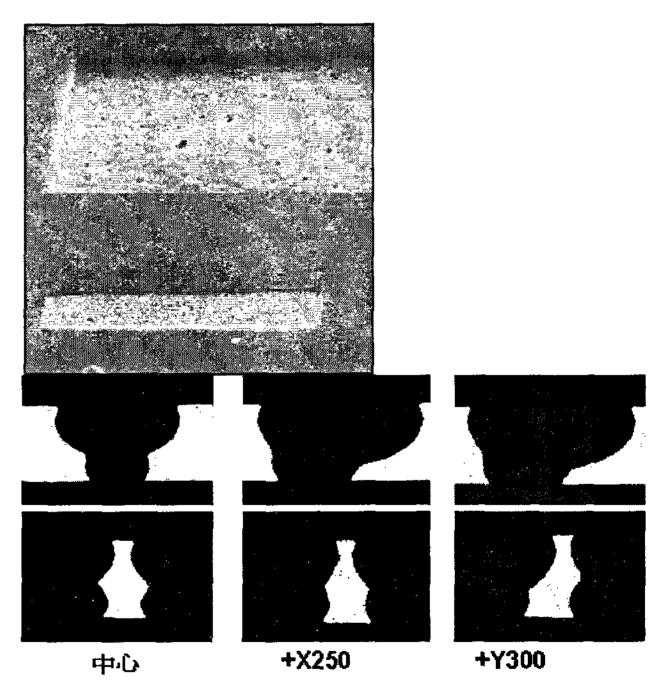




To improve the function of H2O2, we used some organic acids in pre-etching chemistry with H2O2. the fringe of PR is caused of developing water & diffusion of UV exposure so it is weak than normal PR. We searched the breaking chemistry the chain of the fringe of PR. So we know through the test HSO3 & some organic acid help H2O2 break the chain of the fringe of PR.

We can see The result of after treating new chemistry in fig 4).

Fig 4) The appearance of developing hole(SEM) (after treat of new pre-etching chemistry)



As we used the chemistry the quality of fine-pitched shadow mask was increased very fast.

## 3. Conclusion

The materials of new pre-etching chemistry are

combined. The purpose of new pre-etching chemistry is making oxidization of the surface of Fe/Ni alloy and discharge to solution like (Fe<sup>+2</sup>) & (Ni<sup>+2</sup>) form.

We considered to increase the Quality of fine-pitched Shadow-Mask for a long time. We studied about to make sharpness of PR first, after all We find out the method of breaking the fringe of PR. Next we also should have to remove the particle problems

Recently We use the new pre-etching chemistry, also we make good grade of quality in Shadow mask

This study is just a small part of LGM's innovation.

## 4. References

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