

A study of concentrated (98%) H₂O₂: compatibility with Ni alloys and reserve stability of some metal contaminants

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Abstract:

A number of important questions concerning compatibility and stability of 98% H₂O₂ have been investigated. The compatibility of 98% H₂O₂ with nickel alloys was tested and found to be much greater than that of 90% H₂O₂ under the same test conditions. This observation is explained by the hypothesis that an inert protective metal oxide layer formed on the surface of nickel alloys in presence of 98% H₂O₂. No such oxide layer formed when similar coupons were immersed in 90% H₂O₂ solution. Reserve stability of H₂O₂ solution towards decomposition was challenged by adding controlled amounts of five metal cations. With 98% H₂O₂, the order of catalytic activity of them from high to low is Mn²⁺ > Cu²⁺ > Fe³⁺ > Cr³⁺ > Ni²⁺. Trends in stability for doped and undoped H₂O₂ solution were quantified for the first time for the concentration range of 10-98% H₂O₂. The role of pH on stability and the stabilizing capability of stannate were also evaluated. A broad maximum in stability exists over a pH range of 0 to -2.5. Stannate at 2.7ppm Sn provided reserve stability (with no change in measured stability) up to 190ppb of added Fe.

Introduction:

Decomposition of hydrogen peroxide (H₂O₂) almost always occurs due to the existence of impurities⁽¹⁾. These contaminants in commercial peroxide are from the materials contacting H₂O₂ during production, storage, transport and/or application. The rate of decomposition depends on the identity, state and concentration of impurities^(2,3), the effectiveness of stabilization⁽⁴⁾, pH management⁽⁵⁾ and temperature⁽⁶⁾. Thus far, we have only limited knowledge about the decomposition process⁽⁷⁾. Consequently, the study of high concentration H₂O₂ is becoming more and more urgent to meet the increasing demand from aerospace and other applications^(8,9).

The first objective of this work was to evaluate the mutual compatibility of commercial grade 98% H₂O₂ and Ni alloys and the role of catalytic metal ions in their solutions, as metal ions are released from the metal surfaces. Iron-based materials were also tested for comparison. The resulting stability of the H₂O₂ solutions impacts on its safety while being stored, in shipping, and in aerospace applications. Until now, the compatibility of certain common metals with 98% H₂O₂ and the role of metal ions on catalyzing the decomposition of H₂O₂ have not been reported. No studies have been reported on metal catalysis with variables of temperature, pH, H₂O₂ concentration, and metal concentration. Greater knowledge of how these variables influence the rate of H₂O₂ decomposition will ensure its safe and economical use. Therefore, a second objective is to quantify the catalytic role of each of five metal ions, added to the H₂O₂ solutions. The metals are Mn⁺², Cu⁺², Fe⁺³, Cr⁺³, and Ni⁺². These metal ions can be partially deactivated with tin, a stabilizing metal in the form of stannate in the solution. Most of commercial H₂O₂ are stabilized with added chemicals. So, a third objective is to evaluate the role of tin stabilizer on the stability of 98% H₂O₂ solution.

Experimental section:

Material compatibility and H₂O₂ stability were tested in a similar way. The hydrogen peroxide was held in a Pyrex volumetric flask with an extended long neck, so that there was enough room to condense the vapor of H₂O₂ solution, and that gaseous oxygen was the only species that escaped from the flask. The flasks were cleaned and passivated before use. Temperature was controlled with a water bath in which the temperature was maintained within +/- 0.1°C. For compatibility tests, material coupons were immersed in H₂O₂ solution at 66°C for a week. The ratio of coupon surface to H₂O₂ volume is about 0.33 in⁻¹. For stability tests, 50 ml of H₂O₂ solution was maintained at 100°C for 24 hours. Great care was taken during the test to make sure the weight change was only from active oxygen loss without any other contributions.

The analytical values reported after immersion compatibility test include 1) changes in weight and concentration of the hydrogen peroxide solution, 2) changes in weight of material coupons, 3) stability and the concentration of catalytic metals in the exposed H₂O₂ solution. The concentration of the H₂O₂ solution was determined by titration with permanganate solution. The metal contents were analyzed with ARL 3410+ ICP. The relative standard deviation of the ICP analysis is 3 to 10% depending on the metals analyzed.

Water solutions of metal dopants were made from high purity reagents as listed in table 1 in order to minimize cross-impacts when a single metal was tested. The concentration of metal ions in bulk solution was made so that the amount of dopant used in each run was large enough to be accurately weighed, but small enough to render the change in H₂O₂ concentration insignificant. The pH was adjusted by water solutions of high purity sulfuric acid and sodium hydroxide and the pH value was measured with a glass electrode.

Active component	Chemical formula	Purity	Conc. of active component in doping solution
Fe ³⁺	Fe(NO ₃) ₃ ·9H ₂ O	99.99+%	207 (ppm)
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	99.99+%	1033 (ppm)
Cu ²⁺	Cu(NO ₃) ₂ ·2.5H ₂ O	99.99+%	421 (ppm)
Mn ²⁺	Mn(NO ₃) ₂ ·xH ₂ O	99.99+%	131 (ppm)
Ni ²⁺	Ni(NO ₃) ₂ ·6H ₂ O	99.99+%	1014 (ppm)
Sn(IV)	K ₂ SnO ₃ ·3H ₂ O	99.99+%	3206 (ppm)
H ⁺	H ₂ SO ₄	High purity	1:10(H ₂ O)
OH ⁻	NaOH	99.99+%	1:5(H ₂ O)

Assay	98.0min	Stability	98%min	Tin	0.7 – 2.7ppm	Carbon	30ppm max.
Cr	20ppb max	Mn	20ppb max	Cu	20ppb max	Fe	35ppb max
Ni	20ppb max	Ammonium	2.1ppm max	Al	250ppb max	Pb	20ppb max
Cl	0.35ppm Max	Phosphate	0.14ppm Max	Sulfate	0.35ppm Max	Nitrate:	2.1 – 3.5ppm
Particulate	0.6ppm max	Residue	14ppm max				

The 98% HTP grade hydrogen peroxide used in this test was obtained from FMC Corporation's Bayport plant. Unless mentioned otherwise, the assay is 98.62 wt%, stabilizer is 1.15ppm Sn and

trace impurities are all within FMC shipping specifications for 98% HTP H₂O₂, which was listed in table 2. Analyses were conducted by FMC's HTP and electronics quality control laboratory.

Results and discussion:

Material compatibility: The results of compatibility test were shown in the table 3. Four types of material were tested. Two of them, Ni 200 (99.6%Ni) and INCO 625 (minimum 58%Ni, 20-23%Cr), are nickel-based. The other two, A 286 (25%Ni, 14%Cr, 56%Fe) and CRES 347 (11%Ni, 17%Cr, 68%Fe), are iron-based. A blank control test was also run in parallel for monitoring the system contributions to the results. The change in weight and concentration of peroxide solution in presence of coupons was measured, and relative active oxygen loss (RAOL) was calculated from them. In table 3, Δ(AOL(%)) is the difference between sample RAOL and blank RAOL, representing the effect of the coupon on decomposition of the H₂O₂. The metal contents are the amount of metals increased due to the exposure of the solution to the coupon. NID stands for no increase detected, indicating no difference in metal levels between the blank and the sample solution.

Compatibility is measured with three aspects of consideration: the propensity of the metal to be oxidized by H₂O₂; the rate of the metal leaching into the H₂O₂ solution; and the activity of metal both on the coupon surface and in the H₂O₂ solution to catalyze the decomposition of H₂O₂. According to these criteria, it can be seen clearly by comparing table 3A and 3B that nickel alloys are much better compatible with 98% than with 90% H₂O₂.

Table 3A. Compatibility test of metal coupons with 90% HTP H₂O₂ at 66°C for 7 days											
Identification		Results				Increase in metal impurities (ppb)					
Run No.	Materials	H ₂ O ₂ Wt loss(g)	Coupon wt loss(g)	Δ(AOL(%))	Stability	Al	Cr	Cu	Fe	Mn	Ni
G0380-87-33	Blank-3	0.10	----	----	99.09%	----	----	----	----	----	----
G0380-87-35	Ni-200-3	10.27	0.0008	22.91%	71.43%	NID	NID	NID	41	20	5471
G0380-88-37	INCO-625-3	45.38	0.0020	99.80%	----	4	8590	NID	NID	20	18489
G0380-88-39	CRES-347-3	1.96	0.0000	3.84%	95.37%	NID	27	NID	53	NID	34
G0380-89-41	A-286-3	4.23	-0.0002	9.02%	97.35%	NID	31	NID	18	NID	253

Table 3B. Compatibility test of metal coupons with 98% HTP H₂O₂ at 66°C for 7 days											
Identification		Results				Increase in metal impurities (ppb)					
Run No.	Materials	H ₂ O ₂ Wt loss(g)	Coupon wt loss(g)	Δ(AOL(%))	Stability	Al	Cr	Cu	Fe	Mn	Ni
G0380-67-21	Blank-1	0.000	----	----	99.53%	----	----	----	----	----	----
G0380-66-13	Ni-200-1	5.296	-0.0003	9.96%	99.38%	NID	1	NID	1	1	59
G0380-65-9	INCO-625-1	1.086	-0.0005	2.14%	98.28%	NID	230	NID	15	2	93
G0380-65-7	CRES-347-1	4.299	-0.0004	8.24%	98.41%	NID	59	NID	5	NID	15
G0380-66-17	A-286-1	2.565	-0.0005	4.87%	98.96%	NID	52	NID	0	NID	16

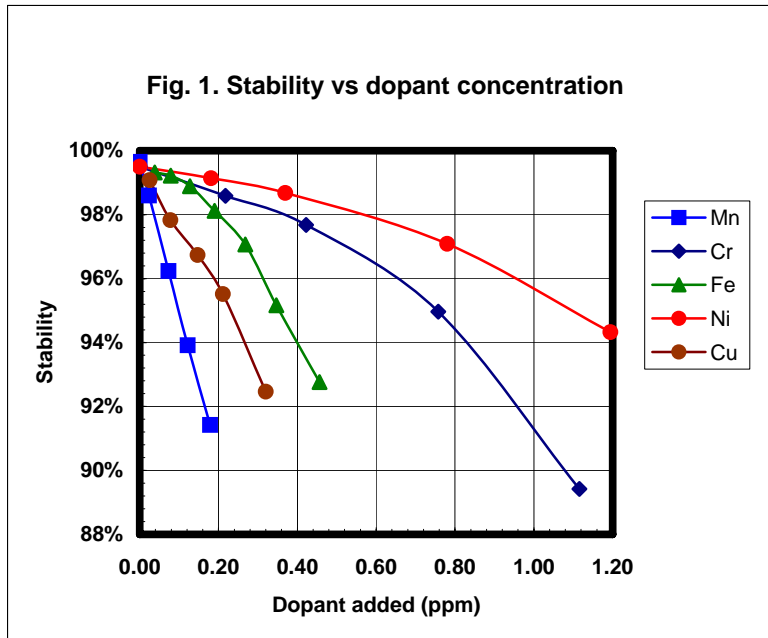
It is well known that some aluminum alloys are compatible with H₂O₂ though its reduction potential is low. An explanation is that an oxide layer formed on the aluminum surface and protected it from further reaction with peroxide. A similar protective layer formed on the surface of nickel alloys in presence of 98%, but not 90% H₂O₂. In 90% H₂O₂, the coupon surface were oxidized and the metals was steadily dissolved into the solution. This was evidenced by the high coupon weight loss and high metal impurity pickup in the H₂O₂ solution. The high active oxygen loss and low stability of the exposed H₂O₂ resulted from the fast decomposition of H₂O₂ catalyzed by the metals released from coupons. In contrast, in 98% H₂O₂ a metal oxide layer

formed on the coupon surface, as evidenced by the gain instead of loss of coupon weight. All other results are also consistent with the hypothesis of the formation of the layer that does not dissolve in the solution: low active oxygen loss, low metal impurities pickup in H₂O₂, and high stability of exposed H₂O₂. It was this layer that significantly reduce the interaction between coupon surface and H₂O₂ solution. Further test on INCO 625 coupons showed that the concentration of H₂O₂ must be no lower than 96% in order for the formation of this protective layer.

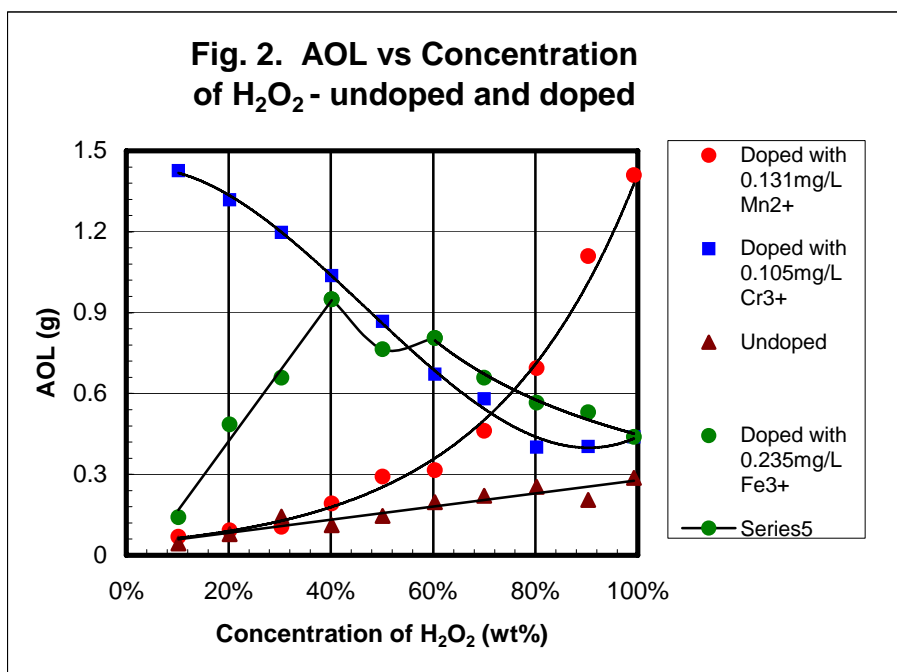
Similar to nickel-base coupons, A 286 coupon is also better compatible with 98% than with 90% H₂O₂ solution. However, the performance of CRES 347 is different. The decomposition of H₂O₂ in presence of this coupon was catalyzed by both metal surface and the dissolved metal ions. And the catalytic activity of coupon surface is higher to 98% than to 90% H₂O₂, since more bubble streams were observed on coupon surface in 98% H₂O₂ solution. As a result, the active oxygen loss of 98% is greater than that of 90% H₂O₂ solution.

Decomposition of H₂O₂: 98% H₂O₂ was doped with five metal ions, and the impact of doping agents on the stability of the peroxide was evaluated. The five selected metals are Manganese (Mn²⁺), Copper (Cu²⁺), Iron (Fe³⁺), Chromium (Cr³⁺), Nickel (Ni²⁺). The stability decreased after doped with each of the five metals. The rate of decomposition increased as the concentration of the metal was increased. The results were shown in Figure 1. The relative catalytic activity of the metal ions can be seen from the position and shape of the curves. The order from most to least active is as follows: Mn²⁺ > Cu²⁺ > Fe³⁺ > Cr³⁺ > Ni²⁺.

It is important to note that the stability of the 98% H₂O₂ solution still remains higher than 90% (the reserve stability with respect to the metals doped), when doped with metal ions at least 10 times higher than FMC shipping specifications. This implies that the reserve stability of 98% H₂O₂ solution is high enough to ensure safety in most applications where exposure time, temperature, and pH regimes are similar to this test matrix.



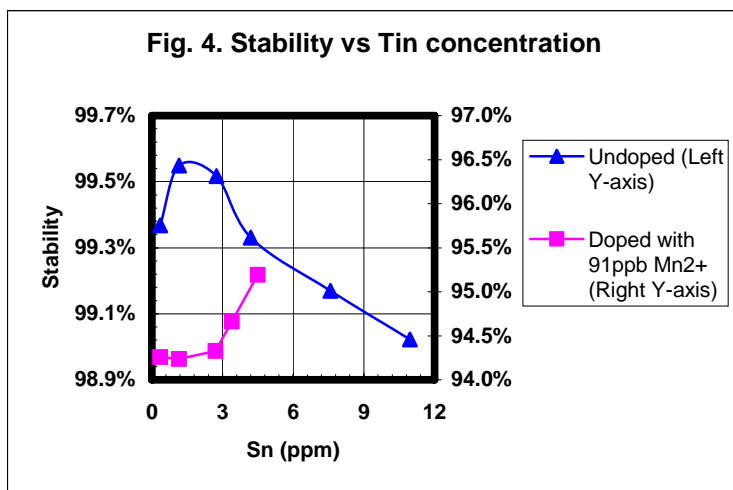
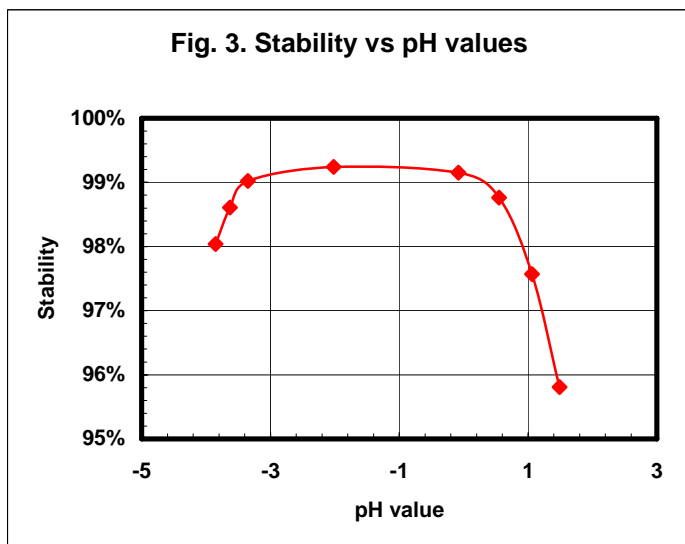
A series of samples were prepared by diluting 98% HTP H₂O₂ with ultra-pure DMW. The resulting concentration range is from 10% to 98%. These samples were tested for impact of dilution factor on the stability, and the results were shown in figure 2. The active oxygen loss (AOL) decreased slightly with the increase in dilution factor. AOL is equivalent to the weight loss in the stability test. The errors from weight lost by evaporation and from the decomposition contributed by metals in the water are negligible.



When doped with each of metals, these samples behave very differently in terms of their stability. From low to high concentration of H₂O₂, the trend of active oxygen loss increased exponentially when the samples were doped with Mn²⁺, decreased significantly when doped with Cr³⁺. The trend for Fe³⁺ doped samples is not straightforward. With increasing concentration of H₂O₂ it increased in dilute portion, and decreased in concentrated part. The inflection points on the curve are informative to the mechanism of Fe catalysis, as they are related to specific molar ratios of H₂O and H₂O₂. Further study about Cr³⁺ and Fe³⁺ catalysis is under way, and the results will be reported separately. Each of these curves can be used to predict the decomposition process in a storage tank based on the metal contaminants in it. For example, it is much more hazardous if high concentrated H₂O₂ solution is contaminated in similar level with Mn²⁺ than with Cr³⁺, and the impact of these two metal ions will be swapped if dilute H₂O₂ is referred. Furthermore, we know that the concentration of H₂O₂ will decrease by decomposition during storage. According to the curves in figure 2, we can predict that the rate of decomposition will decrease when contaminant is Mn²⁺, but will increase when contaminant is Cr³⁺.

It is clear from figure 3 that the addition of either acid or alkali to hydrogen peroxide solutions increases the decomposition rate. Hydrogen peroxide solution is most stable at about, or slightly lower than, its natural pH. The pH of the 98% H₂O₂ used in this test is -0.1, and the highest stability is seen in the range of pH values from -2.5 to 0. It is worthy to note that some surfaces,

especially the surface of corroded container or surface of particle impurity, could change the local pH value of H_2O_2 solution and catalyze the decomposition of H_2O_2 .

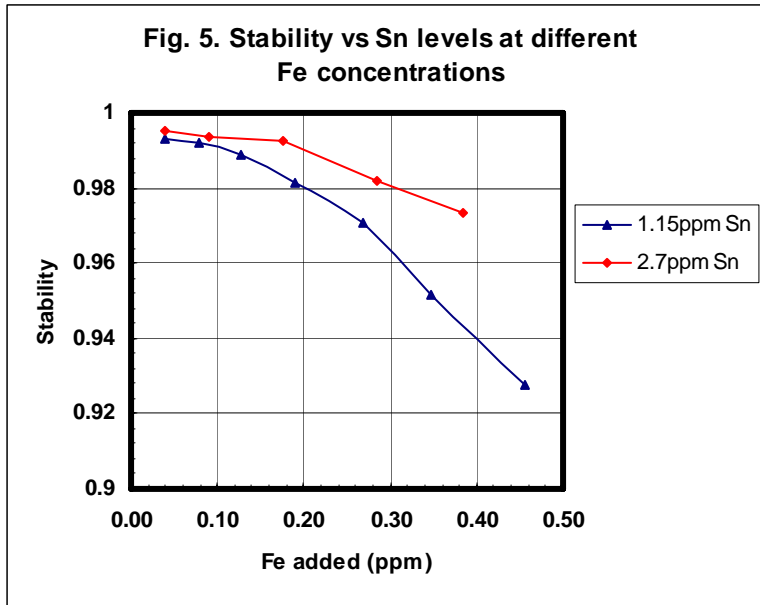


Effects of stabilization: The effectiveness of potassium stannate as stabilizing agent was challenged by measuring the stability of 98% H_2O_2 with various levels of tin and catalytic metals. When stannate was added in increasing amounts to the undoped 98% H_2O_2 solution, the stability initially increased and then slowly decreased. Consequently, there existed an optimum amount of stabilizer, which is about 1.8 ppm of Sn as shown in figure 4. The location of the maximum and the effect of the tin would be different if the metal impurities varies. After the maximum, it is postulated that the hydrolysis of excessive potassium stannate increases the pH of hydrogen peroxide, which results in decrease in its stability.

Mn^{2+} can not be deactivated in 98% H_2O_2 solution until the concentration of Sn exceed a specific level. For example, the stability of the H_2O_2 containing 91ppb of Mn^{2+} was improved only after the addition of Sn was over 3ppm as shown in figure 4. This is consistent with the result of

Mn²⁺ in figure 1, in which the stability is directly proportional to the concentration of Mn²⁺ added, and no stabilization effect on Mn²⁺ can be seen. Therefore, Mn²⁺ is most hazardous to catalyze the decomposition of high concentration H₂O₂ in these five tested metal cations.

On the other hand, Fe³⁺ in the solution can be completely inhibited by Sn. The curve for 2.7ppm Sn in figure 5 is flat as long as the concentration of Fe³⁺ in 98% H₂O₂ solution was no more than 190ppb. The solution containing 2.7ppm Sn is consistently more stable than that with 1.15ppm Sn. Higher concentrations of Fe³⁺ dopant yield a larger difference in the stability. No similar flat portion was seen on curves in figure 1 in which the concentration of Sn stabilizer is 1.15ppm.



Summary:

1. Nickel alloy coupons are much better compatible with 98% than with 90% H₂O₂ solution. An inert layer formed on the coupon surface in 98%, but not in 90% H₂O₂, and protected the coupon from further reactions with the H₂O₂.
2. The order of catalytic activity for the five metal ions from most to least is as follows: Mn²⁺ > Cu²⁺ > Fe³⁺ > Cr³⁺ > Ni²⁺. After 98% H₂O₂ solution was doped with these metals at levels 10 to 60 times higher than FMC shipping specifications, the stability remains higher than 90%.
3. From low to high concentrations of H₂O₂, the trend for active oxygen loss increased slightly for undoped samples. This trend changed dramatically for the samples doped with metals: increasing exponentially with Mn²⁺, decreasing with Cr³⁺.
4. The curve of stability vs pH of 98% H₂O₂ showed maximum stability between 0 and -2.5.
5. The effectiveness of potassium stannate for stabilizing 98% H₂O₂ solution depends on the nature and concentrations of the metal impurities. Though only true to a small degree, excess Sn will destabilize the H₂O₂ solution.

Potential Future studies of value:

1. Test the synergetic effects of different metals on the stability of concentrated H₂O₂ solution with statistically designed experiment. H₂O₂ solution will be contaminated by various

materials that contact with the solution. Its stability will be more accurately predicted, if both individual and synergetic effects of metals are taken into consideration.

2. Test the effects of anions. The impact of anions on the decomposition of hydrogen peroxide can be direct, such as catalyzing or reactive anions, or indirect, such as changing the catalytic activities of metals by complex formations.
3. Test the effect of variations on concentration, pH value, temperature and states of the impurities. They are important for designing containers for storage and transportation. We need guidelines for each of these factors to ensure safety in worst-case-scenarios.
4. Test the effectiveness of stabilizers for high concentration H₂O₂. Proper stabilization of peroxide solution could improve the safety limit and promote applications of H₂O₂.
5. Test the compatibility of materials with concentrated hydrogen peroxide. The compatible materials are essential to maintain the high quality of H₂O₂ products, and the compatibility with 98% could be substantially different from our experiences of compatibility with dilute H₂O₂.

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