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Developments and Properties of Zn-Mg Galvanized Steel Sheet "DYMAZINC" Having Excellent Corrosion Resistance

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Abstract:

"DYMAZINC" (hot-dip galvanized steel sheets having an extra thick and highly corrosive resistant coating) was developed with the objective of extending the longevity of hot-dip galvanized steel sheets. The characteristics of DYMAZINC are that it has a thick coating weight rivaling that of post-dip galvanized steel sheets and that it contains special elements such as Mg in its coating layer. We evaluated characteristics such as its resistance to corrosion and formability and its economic merits to arrive at the basic composition of Zn-0.5% Mg-0.2% Al for the Zn-Mg-Al coating. DYMAZINC has excellent corrosion resistance, particularly in regions where salt damage is problematic. It also withstands surface abrasion that can occur in the forming process because of its superior hard exterior surface. Therefore, this material promises to be an environment-friendly and resource-saving coated steel product.

1. Introduction

Hot-dip galvanized steel sheets are widely used as a material for civil engineering and construction because they have superior resistance to corrosion. Hot-dip galvanized steel sheets use 90 to 300 g/m^2 of Zn plating per side. The speed of corrosion of the zinc coating in regions that have a moderate climatic environment is 5 to 10 $g/m^2/y$, but it is known that in coastal regions, the rate of corrosion is as much as 20 to 30 $g/m^2/y$[1]. In areas that have high chlorine concentrations, there are many cases in which the longevity of galvanized steel sheets is insufficient while in recent years there is an ever increasing demand for an extended longevity because of a move toward maintenance free products. Also, thick galvanizing to the level of 450 to 550 g/m^2 on one side of steel sheets could only be manufactured using a batch type post-processing in which there was the problem of high costs. On the other hand, there are the Nippon Steel's Super Zinc (Zn-5% Al-0.1% Mg) thin galvanized steel sheets that attempted to achieve increased longevity and the Daido Steel Sheet's Galvalume (Zn-55% Al-1.6% Si).

This report outlines the research on Zn-Mg alloy galvanized steel sheets with increased longevity and the development of "DYMAZINC" having an extra thick coating and highly corrosion resistant galvanized plating with the premises that:

- The same manufacturing processes as those for zinc galvanized steel sheets will be used;
- Customers can use them in their manufacturing processes without making unique changes;
- There will be no excessive increase in costs compared with normal zinc galvanizing;
- Corrosion resistance equivalent to post-processing plating will be maintained.

This paper also reports on the corrosion resistance properties of this product.

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2. Determining the Amount of Additional Mg and the Structure of the Plating Layers

It has been known through salt spray testing that the addition of minute amounts of Mg in Zn leads to a dramatic increase in resistance to corrosion[2]. The results are shown in **Fig. 1**[2]. It is clear that an addition of a minimum of 0.3% Mg results in the dramatic increase in corrosion resistance. We decided to set the Mg content to 0.5% by considering the corrosion improvement effect, the operability and economics of this material[3].

Fig. 2 shows a photograph of a cross-section of the plating layer. Because the Zn-Fe alloy layer of the interfacial plane is extremely thin on iron, bend forming is easy. Normally, a primary rust-proofing such as a special chromate treatment is performed for use.

3. Experimental Procedures

3.1 Procedures used to prepare specimen

After pickling commercial hot-rolled sheets, we used our automated galvanize plating apparatus to hot-dip galvanize the steel sheets in the bath (450°C) with an Mg concentration of 0.5%, Al concentration of 0.2 to 0.3% and the remainder being zinc to create the specimen. The deposit was controlled using gas wiping to conform to 150 g/m^2. We used pure zinc galvanized steel sheets with the same deposit for comparison.

3.2 Corrosion resistance evaluation

Our study of the corrosion resistance of specimens included: 1) salt spray testing (abbreviated to SST below); 2) atmospheric exposure testing (Nippon Steel Hirohata Laboratory's Exposure Yard and Idemitsu Industries Aichi Oil Refineries); 3) atmospheric corrosion promotion procedures (a method that sprays 5% Nacl twice a week) and 4) compound cycle corrosion testing (CCT use a cycle of salt spray, drying, wetting and drying). We measured the weight reduction for the sample after removing the corrosion product using a chemical treatment (2% CrO_3 + 12.5% NH_3). For structural analyses, we mainly used the optical microscope and SEM-EDA. In order to grasp the behavior of the corrosion, we took X-ray analysis and electro-chemical measurements after the corrosion testing.

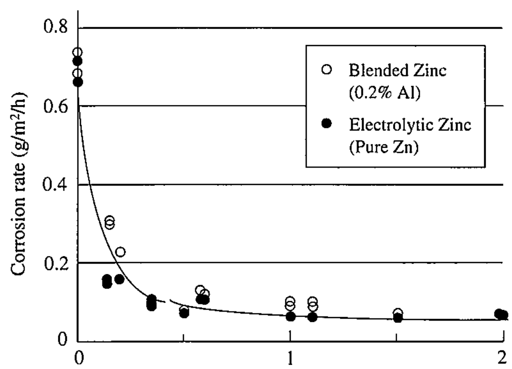


Fig. 1 The Relationship of the amount of Mg added and corrosion resistance

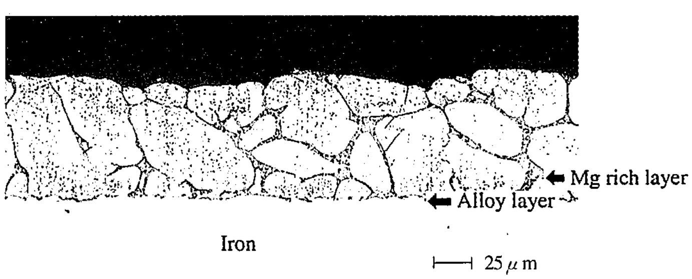


Fig. 2 Cross-sectional photograph of Zn-0.5% Mg plating layer (single-side 450 g/m^2)

Table 1 Paintability testing results list

Materials: Zn-0.5% Mg plated steel sheets (unprocessed)

	Chemical	Items of evaluation	Evaluation
Chemical processability	Phosphoric acid zinc processing PB3113*1	Film weight Existence of scale	Pass None
Paintability	Chemical(PB3113) + Acrylic Powdered paint	Base visual test Withstanding boiled water test Withstanding blister test	100/100*3 100/100 None
	Primer: Urethane variable epoxy (P01*2) Top coat: Polyester base paint (NSC655*2)	Base visual test Withstanding boiled water test Withstanding blister test	100/100 100/100 None

*1 Made by Nihon Parkerizing Co., Ltd.
*2 Made by Nippon Paint Co. Ltd.
*3 Residue rate/base visual count

3.3 Scratch resistance evaluation

We slid 10 mm steel ball (100 gf load) using a Haydon friction coefficient measuring device over the surface of the steel sheet 10 times, then we measured the friction coefficient on the tenth time. At the same time, we also measured the hardness of the surface.

3.4 Painting performance

We evaluated painting performance of the steel sheet shown in **Table 1** using a conventional processing agent.

4. Results of the Experiment

4.1 Corrosion resistance testing

4.1.1 SST corrosion resistance

Fig. 3 shows the plating deposit that was adhering to one side and the time until rust occurred. You can clearly see that Zn-Mg plated steel sheets have superior corrosion resistant qualities.

Fig. 4 shows a photograph of the external appearance of a product with Zn-Mg plating and a product that underwent post-processing (both are one sided 450 g/m^2; sheet thickness 4.3 mm) with 1,000 hours of SST. There is absolutely no rust on the Zn-Mg plated steel sheet on the flat surface and in the cross-sectional view, the Zn-Mg corrosion product covers the iron, thereby reducing the corrosion of the iron.

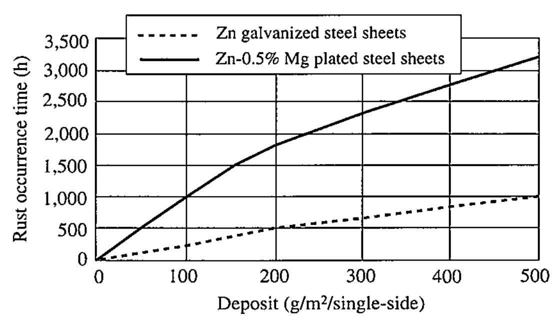
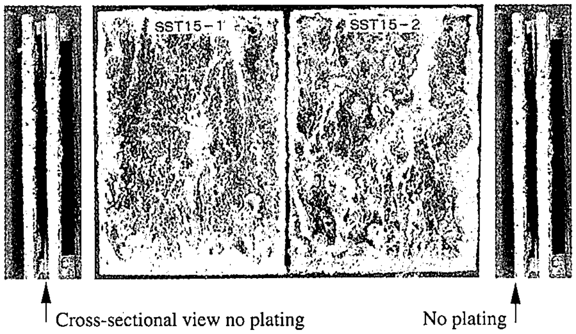
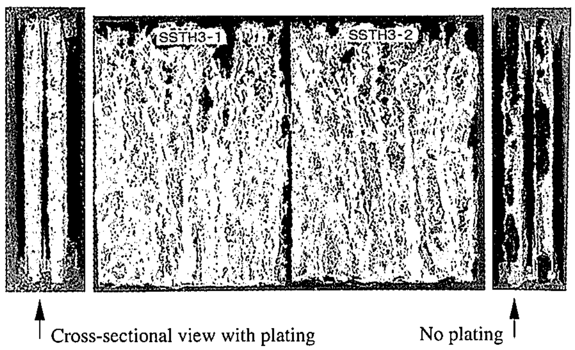


Fig. 3 Effects of plating deposit on SST corrosion resistance



(a) Zn-0.5% Mg plated steel sheets



(b) Post-galvanized steel sheets

Fig. 4 Photograph of external appearance after 1,000 hours of SST (each photograph shows two steel sheets.)

4.1.2 Atmosphere exposure testing

Figs. 5 and **6**[4] show the results of the exposure testing performed at the Nippon Steel Hirohata Laboratory's Exposure Yard and Idemitsu Industries Aichi Oil Refineries. As can be clearly seen in the figure, Zn-Mg layers has superior corrosion resistance in the actual environment and the exposure testing. Further, both the exposure testing and the actual environment are areas with an extremely high annual average chlorine concentration of 0.5% in rain fall and with a moderate climate. This indicates that in either case, Zn-Mg plating has superior corrosion resistance qualities.

4.1.3 Atmosphere promoted corrosion testing

Fig. 7[5] shows the corrosion reduction for the Zn-Mg plated steel sheets and Zn galvanized steel sheet in the atmosphere promoted corrosion testing (sprayed 5% NaCl: twice/week). This figure shows that the Zn-Mg plating is superior when compared to Zn galvanized. In other words, there was only approximately 50 g/m^2 of corrosion reduction over a 10 month period of Zn-Mg plating when there was more than 150 g/m^2 of corrosion reduction over a three month period for Zn plating and rust had developed. Also, it was clarified that the rate of corrosion of Zn-Mg decreased as time elapsed.

To uncover the cause of this phenomenon, we performed a cross-section analysis of the corrosion product. **Fig. 8** shows the results. The corrosion product was extremely thin and dense on the Zn-Mg plating. We inferred that a protective effect of the film on the corrosion product prevented the infusion of water and Cl^- which are the causes of corrosion. Thus, Zn-Mg plating layers were inferred to have superior corrosion resistance qualities.

Furthermore, we observed a cross-section of a 2.0 mm thick steel sheet (see **Fig. 9**). When there was a layer of Zn-Mg plating

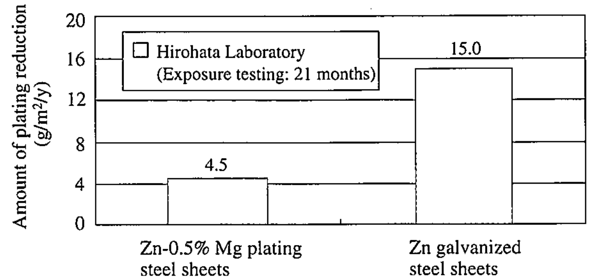


Fig. 5 Amount of corrosion reduction of plating in the atmosphere exposure test

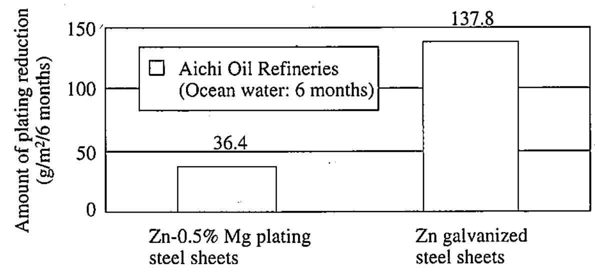


Fig. 6 Amount of corrosion reduction of plating in the atmosphere exposure test[4]

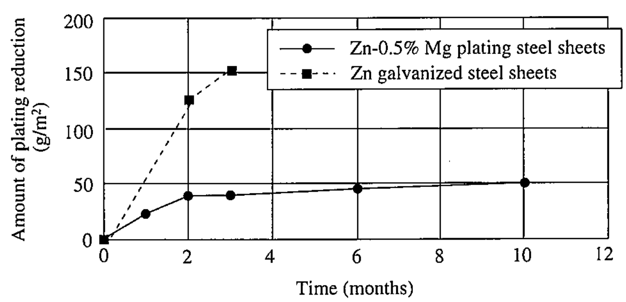


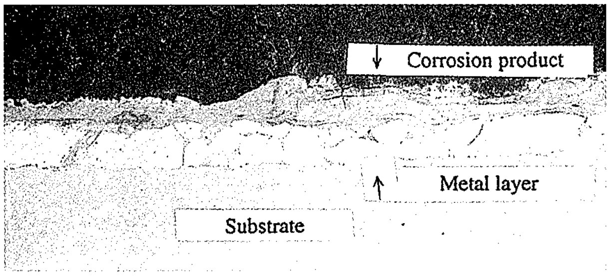
Fig. 7 Amount of corrosion reduction of plating in the atmosphere exposure test[5]

on the flat side, a mild degree of rust developed in the initial stages, but soon the corrosion product protective film covered the Fe exposed sides which had the affect of protecting those Fe exposed parts. **Fig. 10** shows a model of the change over time.

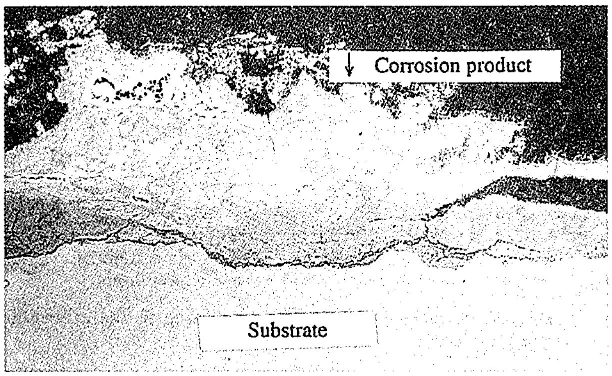
4.1.4 Compound corrosion cycle testing and corrosion product analysis

Fig. 11 shows the results of the corrosion cycle testing in which we received the same results. In other words, the corrosion reduction of Zn-Mg plating was approximately 1/5 compared to Zn plating.

To understand the causes for the superior corrosion resistance qualities of Zn-Mg plating, we used the testing material after 5 cycles of CCT, and found that while the oxidized zinc (ZnO) was the main corrosion product in Zn plating, the corrosion product was lower in Zn-Mg plating and that the basic zinc chloride ($ZnCl_2 \cdot 4Zn(OH)_2$) ratio was high (see **Fig. 12**). Furthermore, the results of our investigation of the polarizing characteristics of the corrosion product of the same specimens showed that cathode reactions (oxygen reducing reaction) were more suppressed in Zn-Mg than in Zn plating (see **Fig. 13**)[6]. We think that this is caused by the denseness of the corrosion product (see **Fig. 8**) and the difference in their compositions.



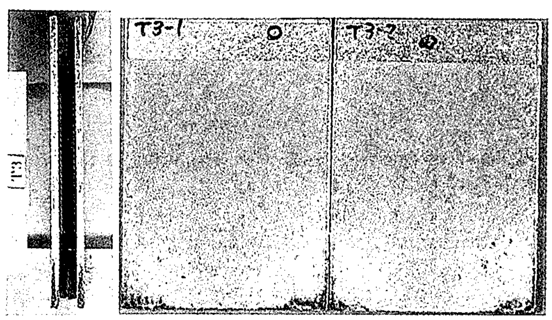
(a) Zn-0.5% Mg plated steel sheets



10μm

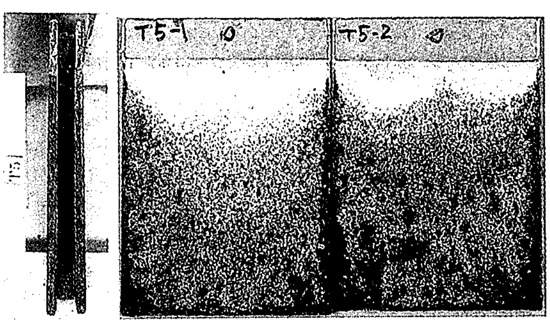
(b) Zn galvanized steel sheets

Fig. 8 Photograph of a cross-section of corrosion product (after one month of atmospheric promoted exposure testing)[5)]



Cross-section

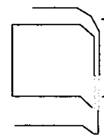
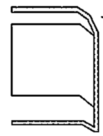
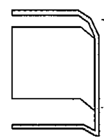
(a) Zn-0.5% Mg plated steel sheets



Cross-section

(b) Zn galvanized steel sheets

Fig. 9 External appearance after corrosion (after nine months of atmospheric promoted exposure testing; sheet thickness: 2.0 mm)

Initial term (five days and beyond)*		← Plating layer ← A thin layer of rust occurs because there is no plating.
Mid term (six months to three years)		← Dense protective film (white/gray colored) Zinc has become a dense protective film to cover surface.
Long term (over three years)		← Corrosion advanced Rust appears as the protective film dissipates. However, there is a continuation of the corrosion prevention by the flat sided plating that restricts the advancement of the corrosion.

* Years in the parentheses are assumed in atmosphere exposure.

Fig. 10 Changes of corrosion in the cross-section over time (a model)

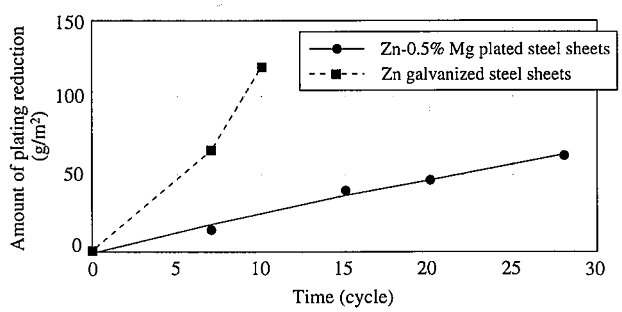


Fig. 11 Amount of plating reduction in CCT

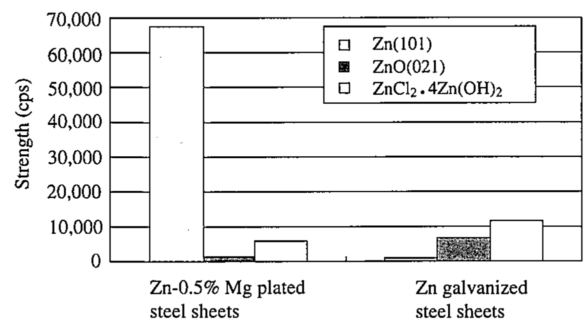


Fig. 12 X-ray analysis results of ccorrosion product (after 5 CCT cycles)

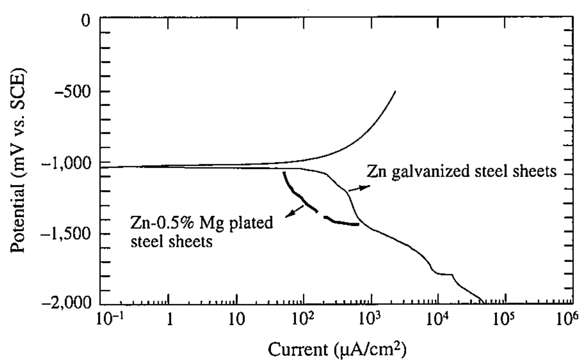


Fig. 13 Polarization curve of corrosion product (after 5 CCT cycles)

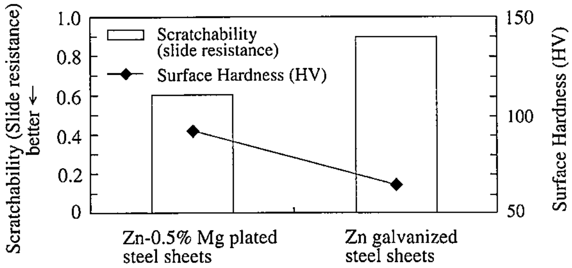


Fig. 14 Scratch resistance on developed product (slide resistance)

4.2 Formability

In the ball impact test and 1T - 2T bending test, formability is equivalent to normal zinc galvanized steel sheets because the Zn-Fe alloy layer is extremely thin.

Further, **Fig. 14** shows the results of our evaluation of scratch resistance (slide resistance) using friction coefficient measurements. Because Zn plating is a soft metal, a part of the plated surface is gouged during the tube manufacturing process. Because the surface of the Zn-Mg plated product is hard, it is difficult to be gouged which indicates that it has the quality of being difficult to damage.

4.3 Paintability

Table 1 shows the results of our paintability testing. This showed characteristic equivalent to current hot-dip Zn plating. It is possible to paint without particular equipment changes.

4.4 Establishing thick plating manufacturing engineering

Along with the improved corrosion resistance of the steel sheets themselves attained through the addition of Mg, we studied plating deposit for single side adhesion over 450 g/m^2 that had been impossible to manufacture on current continuous lines. In the case of pre-plated steel sheets manufactured on these continuous lines, there were many cases in which post-processing occurred after the plating and this requires that the flaking of the plating due to the progress of the Zn-Fe alloying is held to a minimum. We shortened the dip plating time (1 to 3 seconds) which allowed for the thickening of the plating as a pre-plated steel sheet.

5. Conclusion of Characteristics

- Enhanced longevity by an improvement of corrosion resistance for hot-dip Zn-Mg plated steel sheets in a variety of corrosive environments including the actual environment was possible.
- The corrosion product on hot-dip Zn-Mg plated steel sheets was thin and dense and because the composition was mainly basic zinc chloride, cathode reactions were restricted and corrosion resistance improved.
- Because the hot-dip Zn-Mg plated steel sheets have improved surface hardness, there is a reduction in the amount of scratches during processing and it therefore has superior scratch resistant qualities.
- It is possible to paint hot-dip Zn-Mg plated steel sheets using painting processes used for current hot-dip galvanized steel sheets.
- By restricting the progress of Zn-Fe alloying, we achieved a process in which thickening is possible.

6. Products

We have created a product that has thick hot-dip Zn-Mg plated steel sheets noted below.

Product name: DYMAZINC

Table 2 Plating deposit

Code of plating deposit	Double-sided minimum deposit (g/m^2)
M45	450
M90	900
M110	1,100

Table 3 Market usage of this steel sheet

Field	Main usage	Rating	Market size (t/month)
Civil engineering	Fit Frame	Replacement for concrete	1,200
	Wind/snow prevention fence		500 - 700
Electrical communication	Cable racks	Replacement for post-plating	1,000
Construction material	Expand metal Metals, etc.	Replacement for post-plating Replacement for construction wooden material	2,000

Product description:
Type: See **Table 2**
Sheet thickness: 1.2 to 6.0 mm
Grade: Commercial grade, structural grade (340 - 500 MPa class)

7. Target Market

We have been conducting market opening usage as a test product since July of 1997. It is clear that we can expect demand in the markets shown in results **Table 3** and there are already several companies that have decided to use this product. Other than a replacement for the post-process plating, which is what we had expected for its use from the outset, we see promising demand as a replacement for concrete and wood materials.

8. Conclusion

Attaining the improvement of corrosion resistance of the plating layer itself for a demand for enhanced longevity in the civil engineering and construction materials fields and the thickening of the plating that had been difficult to manufacture with the current low costs are the features of this technology. These steel sheets can be welded and we also expect that there will be an expansion into various fields in the future. We think that it is also necessary to gather exposure testing data in a variety of environments.

9. Acknowledgments

We wish to express our thanks to Mr. Takashi Yashiki of Idemitsu Industrial for the use of the atmosphere exposure testing facilities and Mr. Hiroyasu Ishimoto of Idemitsu Engineering for their cooperation in our research.

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