# Variables Influencing Microflocculation in Coalesced Emulsion

Toronto Society for Coatings Technology

*One of the problems associated with coalescing higher glass transition temperature ($T_g$) emulsions is the potential formation of microflocculation. This can have a major impact in the manufacturing filtration process and subsequent application when applied by spray. An experimental screening design was run to study the possible effects of three manufacturing variables and three formulation variables. For this study a higher $T_g$ styrenated acrylic was tested. Results showed the formulation variables to have a significant effect on microflocculation while the manufacturing process variables did not.*

## INTRODUCTION

Waterborne industrial emulsions are finding their way into more and more end uses as the technology improves. Higher glass transition temperature ($T_g$) acrylic emulsions are making inroads in wood coatings as well as high-end metal coatings. Styrenated acrylic emulsions serve well as metal coatings in various end uses including primers. An advantage of higher $T_g$ emulsions is that they give harder films that are more resistant to blocking and mar. The downside of these emulsions is that they are harder to coalesce, and the manufacture of these coatings can be more difficult.

When applying films at room temperature, the coating needs to be coalesced through the use of plasticizers and/or solvents. Plasticizers are efficient in lowering the minimum film forming temperature below application temperature, however, they remain in the film and render the film soft and susceptible to blocking. Using slow evaporating solvents as the means of coalescence will eliminate the problems associated with plasticizer yet they come with their own problems. When using solvents as a means of coalescence, the VOC of the coating is increased as compared to emulsions with lower $T_g$s that require little or no solvent in the formulation. In earlier years coalescing solvents readily used ethylene-based glycol ethers (E-series). These are considered hazardous air pollutants (HAPs) and are undesirable due to health related issues. The past few years have seen an increased use of propylene-based glycol ethers (P-series) that are not considered HAPs and are considered better from a toxicology standpoint. Practical experience has shown that P-series solvents are not easy formula replacements for E-series.

A problem associated with using higher $T_g$ emulsions that has not received a lot of attention in the literature is the greater difficulty in manufacturing these coatings due to emulsion shock or kickout. This shock or kickout can take place on a macro scale as exhibited by grit that is easily visible to the naked eye. The kickout can also be on a smaller scale that is not visible to the eye. These small size gels are unlike micro gel particles that are used in various end uses as shear thinning dispersions.[1] Microflocculation is best defined as the clumping together of polymer particles into a larger particle. If the microflocculation is bad, the coating will appear to be full of grit or even worse, kicked out. Literature on microflocculation is not readily available, perhaps because it is often dealt with on a manufacturing level. However, if these small size gels are not eliminated properly at the coatings manufacturing level, they can play a significant problem in certain end uses such as spray coatings. If emulsion coatings that still contain microflocculant are sprayed, guns could easily clog causing unnecessary manufacturing down time for the customer.

The Toronto Society for Coatings Technology (TOSCOT) undertook as a challenging project the study of microflocculation as it pertains to coalesced emulsion. The objective was to identify potential variables that might lead to problems with grit or small size gels and how this problem might be minimized.

A preliminary literature search on the subject of emulsion kickout or flocculation during coalescence (coating manufacturing stage) revealed little relevant data. An expanded search including the broader topic of film coalescence was more helpful.[2-11] From this search, a hypothesis was developed around these formulation variables which might play a significant role in emulsion coalescence. These included the effects of base, surfactant, and coalescing solvent type.

## EXPERIMENTAL

The TOSCOT Technical Committee narrowed down the study of microflocculation to six key variables. The first three variables were manufacturing related and included mixer blade type, mixer agitation speed, and rate of coalescent addition. Blade types varied between a sharp tooth Cowles blade and a low shear prop blade. These blades were chosen in order to study the effect of shear action on the formation of potential kickout. Mixer agitation speed was chosen as it also related to increased shear on the emulsion. A variation of mixer speed combined with differing rate of coalescent addition hopefully would show what effect if any a buildup of coalescent would play in flocculation of the emulsion. The remaining three variables were formulation related and included emulsion pH,

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**Table 1—Study Variables**

| Factor | Name | Design Levels Low | High |
|---|---|---|---|
| A | Mixer blade type | Prop | Cowles |
| B | Mixer agitation speed (RPM) | 300 | 1200 |
| C | Rate of coalescent addition (Sec) | 10 | 300 |
| D | Emulsion pH | 7.7 | 9.0 |
| E | Emulsion stabilizer (% on TRS) | 0.0 | 1.0 |
| F | Coalescent blend type | Hydrophobic | Hydrophobic/Hydrophilic |

**Table 2—Control Formulation**

| | + Grams | - Grams |
|---|---|---|
| Styrenated Acrylic Copolymer ($T_g$ = 40°C) | 85.75 | 85.75 |
| Defoamer | 0.13 | 0.13 |
| Water } Premix | 0.80 | — |
| Ammonia } | 0.20 | — |
| Water } Premix | 3.47 | — |
| Surfactant } | 0.39 | — |
| Glycol ether PnB } Premix | — | 6.00 |
| Glycol ether PPh } | — | 3.22 |
| Glycol ether PPh } Premix | 3.22 | — |
| Glycol ether DPM } | 6.00 | — |

emulsion stabilizer level, and coalescent blend type. A summary of all six variables is shown in *Table* 1. Due to the number of variables and the uncertainty of their significance in causing microflocculation, a screening experiment was designed. Testing was done using a six factor, two level, half fraction-high resolution design utilizing 32 experiments. The details of the actual design are found in *Appendix* 1.

The control formulation (see *Table* 2) was developed using a styrenated-acrylic emulsion with a $T_g$ of approximately 40°C. This emulsion was chosen because of its known low surfactant/stabilizer level and potential grit formation. The surfactant used in the study was a nonionic block copolymer of propylene oxide and ethylene oxide. The coalescent solvents chosen were P series glycol ethers that have shown use as emulsion coalescents in the literature.

At the start of this project there was concern as to whether suitable testing could be established that would accurately evaluate the role of different variables in causing microflocculation. It was decided that the best method of checking for any microflocculation would be via quantitative filtration. A standard 600 g amount of sample was quickly poured into a 25µ felt filter of known weight. The time it took the sample to drain through was measured as well as the final amount left in the filter.

Additional testing was done to see if microflocculation had any effect on sample viscosity, gloss, and appearance. Gloss and appearance were checked on air dried 1 mil DFT drawdowns over cold-rolled steel Q-panels. Finally, accelerated testing was done on 1.0-1.4 mil DFT Q-panels that had air dried a minimum of one week. See *Table* 3 for a summary of all the tests run.

## RESULTS AND DISCUSSION

The time it took each 600 g sample to pass through a 25µ filter was plotted on a half-normal plot as provided by the design of experiment software (see *Figure* 1). The purpose of the half-normal plots is to check the variables for statistical significance. In testing for the filtration rate, the best results of the half normal plot were obtained using a natural log transformation for the data as expressed in seconds required to pass through the filter. Points furthest from the straight line indicate significant variables. It comes as little surprise that variable F (coalescent type) has a significant effect on ease of filtration. Other significant variables are D (emulsion pH) and E (emulsion stabilizer). One might have predicted that the design and high mechanical shear of the Cowles blade would contribute to formation of kickout and slower filtration. Test data did not bear this out. Surprisingly this study also did not show quick addition of coalescent or slow agitation to contribute to slower filtration rate.

**Table 3—Tests Run**

(1) Ease of filtration
(2) Amount of retained filtrate
(3) Sample viscosity
(4) Film appearance
(5) Cleveland humidity (ASTM D 4585) 385 hr
(6) Salt spray (ASTM B117) 168 hr
(7) Cyclic Prohesion (ASTM D 5894-96) 400 hr

The half-normal plot while indicating variables that are significant does not give a clear picture of which direction is desirable. In *Figure* 2 the ease of filtration for the three formulation variables are plotted in three dimensions in regard to their natural log time response in seconds. In this case the lower the number the better the results, indicating less time to filter the sample. As can be seen, the point representing D+, E+, F+ gives the best result. This shows that the samples with higher pH, stabilizer in the emulsion and hydrophobic/hydrophilic coalescent solvent blend PPh:DPM gives the quickest filtration rate. The TOSCOT Technical Committee felt the ease or lack thereof for filtration rate showed high probability of correlation as to whether gels or microflocculant were being formed. In other words, higher pH, emulsion with stabilizer, and use of a hydrophobic/hydrophilic coalescent solvent blend would give less tendency to cause formation of microflocculation in the emulsion.

To further test for verification of the significant factors that might cause small size gels, the amount of retained filtrate for each sample was plotted on a half-normal plot. These results were measured as the natural log of the grams of increase on a pre-weighed 25µ filter. Results were very similar to what was found in the ease of filtration testing. The half-normal plot showed variable F (coalescent blend) to be highly significant. Also significant but to a lesser extent was the use of emulsion stabilizer. When the natural log results of the three formulation variables were plotted, the point of least retained filtrate was D+, E+, F+. This corresponds directly with the point of quickest filtration.

Three other physical properties were plotted for significance. A summary of these results are found in *Table* 4. Lowest viscosity samples followed the pattern of best filtration and least retained filtrate with higher pH, emulsion with stabilizer and hydrophobic/hydrophilic coalescent being the best. Gloss was tested on CRS drawdowns. The only significant variable for gloss was type of coalescent blend. Highest gloss was obtained using only the hydrophobic blend of solvents PnB:PPh. Appearance of the samples was determined by the degree of seediness and cracking found on an air dried CRS panel. Computer analysis of the appearance results showed no variables to have statistical significance.

The remainder of the tests carried out consisted of accelerated testing in Cleveland humidity (ASTM D 4585), salt spray (ASTM B117), and cyclic Prohesion (ASTM D 5894-96). Analysis of the salt spray and cyclic Prohesion half-normal plots showed the study variables to have no significant effect on performance. In Cleveland humidity the variables under study had a much greater significance on performance. By far the best water resistance was obtained with samples containing no stabilizer and containing only a hydrophobic blend of coalescing solvents.

Subsequent to the completion of this test data, opportunity was made available to the TOSCOT Technical Committee for sample analysis using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Due to limited equipment availability, one sample considered to have the least microflocculant (clean sample) was submitted versus another sample that showed the highest degree of microflocculation (gel sample). Testing by this independent lab verified the technical committee's experimental observations. *Figure* 3 shows an AFM with the clean sample at the top and the gel sample on the bottom. Pictures show the gel sample to have higher protrusions than the clean sample. Of even greater interest is the results obtained by SEM. *Figure* 4 is a 25,000 power magnification SEM with the clean sample at the top and the gel sample on the bottom. This picture clearly shows a greater emulsion particle flocculation with the gel sample as compared to the clean sample. While one AFM and one SEM cannot be considered conclusive support of the TOSCOT findings, they certainly help us to visualize microflocculation.

As seen by experimental filtration results, higher pH improved antiflocculation properties. This may possibly be due to the $NH_4^+$ charge stabilization when incorporating ammonia into the formula. Results also showed higher nonionic block copolymer stabilizer to improve antiflocculation. It is reasonable to believe that the increased surfactant would improve steric stabilization of the emulsion particles, hence less microflocculation. Why the blend of hydrophobic/hydrophilic (PPh:DPM) coalescent solvent gave less microflocculation than the straight hydrophobic blend of PPh:PnB is uncertain. Most likely the blend of hydrophobic coalescing solvents has too quick a partitioning time into the polymer phase versus the coalescing blend containing DPM which would be drawn into the continuous water phase.

When formulating coatings, compromises in properties usually are the norm. This study bears this out when looking at all the tests run. The results show that the coatings with the least gel flocculation have the poorest water resistance. In cases where a metal coating with a high level of water resistance is required the compromise caused by incorporating water sensitive surfactant or slow evaporating hydrophilic solvent could be considerable.

The TOSCOT Technical Committee study ends here with questions unan-

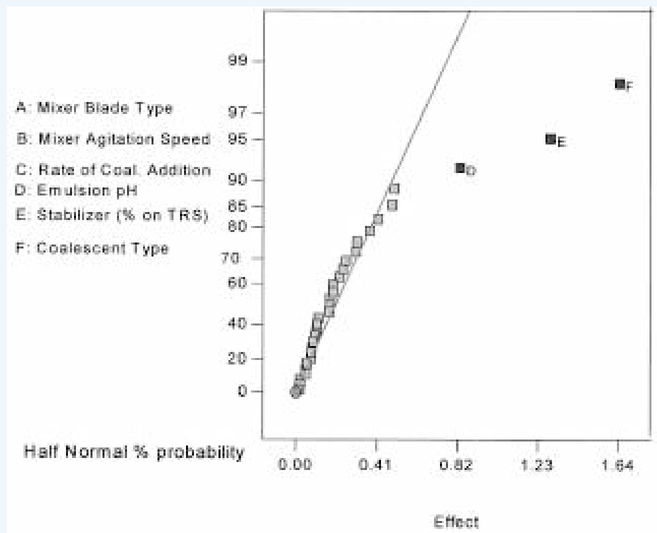


*Figure 1—Design expert: Half normal plot—natural log (ease of filtration).*

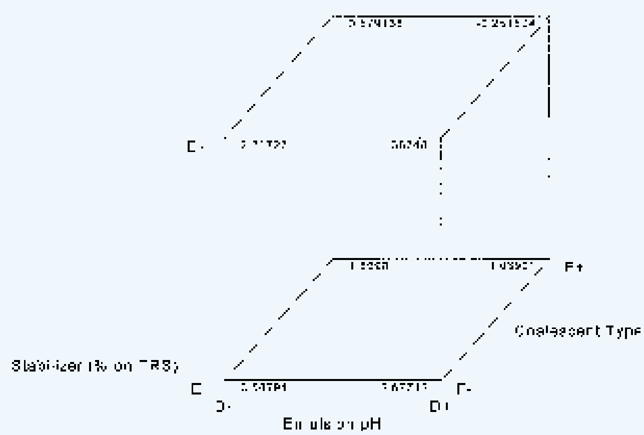

*Figure 2—Design-expert plot: Predicted natural log (ease of filtration).*

**Table 4—Significant Variables for Optimized Results**

| | pH | Stabilizer % on TRS | Solvent Type |
|---|---|---|---|
| Best Filtration .................... | 9.0 | 1.0 | Hydrophobic-hydrophilic |
| Least retained fitration ... | — | 1.0 | Hydrophobic-hydrophilic |
| Lowest viscosity ................ | 9.0 | 1.0 | Hydrophobic-hydrophilic |
| Highest gloss ..................... | — | — | Hydrophobic |
| Best appearance ........... | — | — | — |
| Best Cleveland humidity | — | 0.0 | Hydrophobic |
| Best salt spray .................. | — | — | — |
| Best cyclic Prohesion ...... | — | — | — |

swered. Exactly how the solvent blends work to minimize gel flocculation is uncertain. The issue of reducing or eliminating microflocculation without compromising other key properties remains for another study.

## CONCLUSIONS

The Toronto Society for Coatings Technology Technical Committee studied the factors that might lead to microflocculation of emulsion particles when being formulated into a clearcoating. A higher $T_g$ styrenated acrylic emulsion was evaluated with six variables, both manufacturing and formulation analyzed using a factorial screening design. Results indicated that the primary effect on reducing microflocculation or small size gels was by using a blend of hydrophobic/hydrophilic coalescing solvents rather than a hydrophobic blend of solvents. Use of nonionic surfactant and increased pH also helped to a lesser extent to reduce microflocculation. Other physical properties including accelerated testing were evaluated as well. Test results indicate potential compromise of water resistance properties when formulating to eliminate microflocculation.

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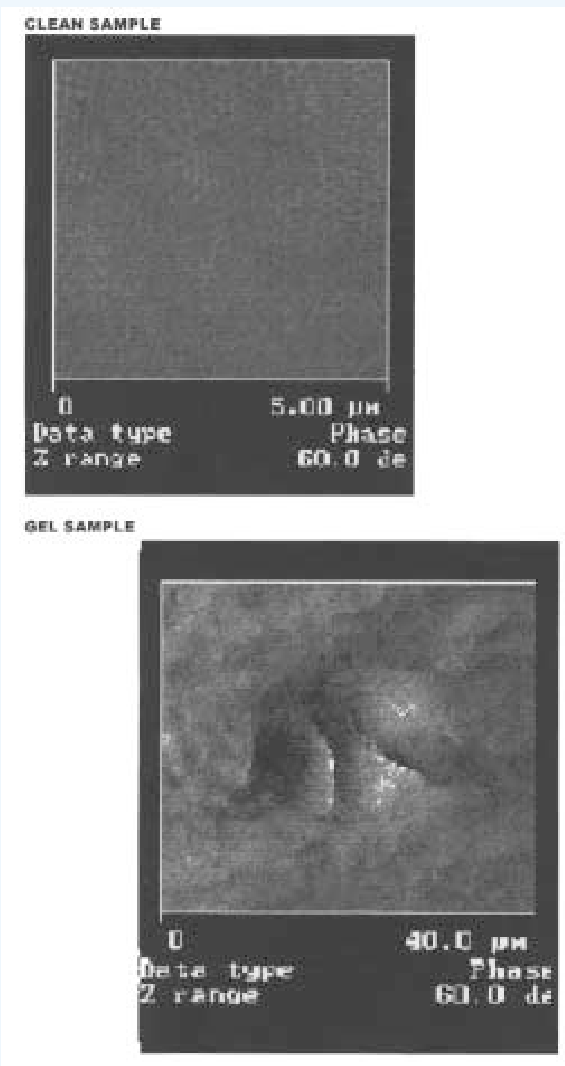


Figure 3—Microgel study atomic force micrograph.

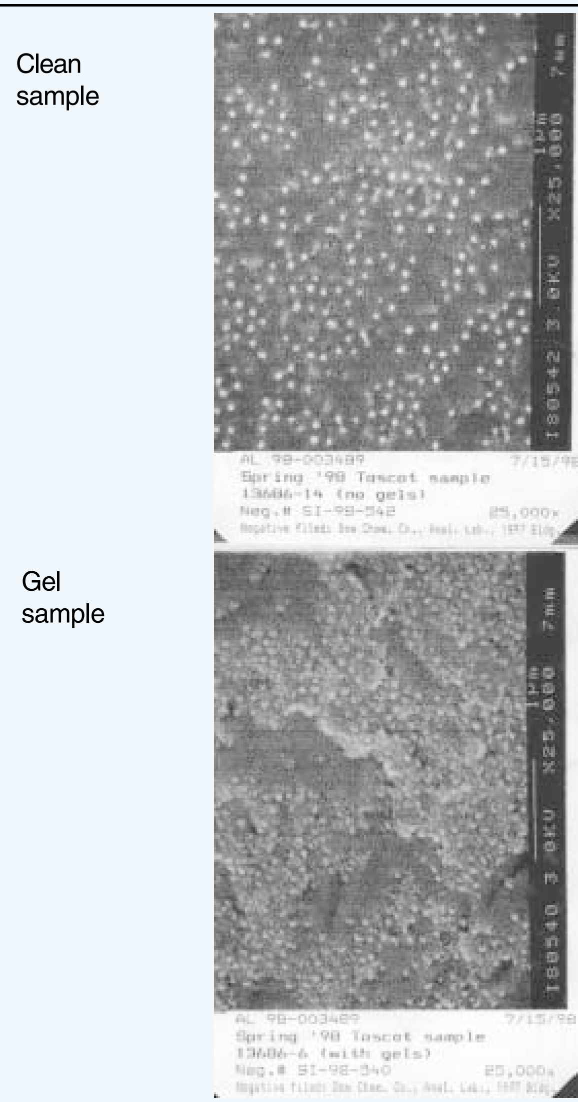


Figure 4—Microgel study scanning electron micrograph.

## Appendix 1—Microflocculation Design Parameters

| Std | Run | Factor A Mixer Blade | Factor B Mixer Speed (RPM) | Factor C Rate of Add. (Sec) | Factor D Emulsion pH | Factor E Stabilizer % on TRS | Factor F Coalescent Type |
|---|---|---|---|---|---|---|---|
| 7 | 1 | Prop | 1200 | 300 | 7.7 | 0 | Phobic |
| 16 | 2 | Cowles | 1200 | 300 | 9 | 0 | Phobic |
| 1 | 3 | Prop | 300 | 10 | 7.7 | 0 | Phobic |
| 22 | 4 | Cowles | 300 | 300 | 7.7 | 1 | Phobic/Philic |
| 15 | 5 | Prop | 1200 | 300 | 9 | 0 | Phobic/Philic |
| 20 | 6 | Cowles | 1200 | 10 | 7.7 | 1 | Phobic/Philic |
| 24 | 7 | Cowles | 1200 | 300 | 7.7 | 1 | Phobic |
| 5 | 8 | Prop | 300 | 300 | 7.7 | 0 | Phobic/Philic |
| 29 | 9 | Prop | 300 | 300 | 9 | 1 | Phobic/Philic |
| 17 | 10 | Prop | 300 | 10 | 7.7 | 1 | Phobic/Philic |
| 11 | 11 | Prop | 1200 | 10 | 9 | 0 | Phobic |
| 31 | 12 | Prop | 1200 | 300 | 9 | 1 | Phobic |
| 9 | 13 | Prop | 300 | 10 | 9 | 0 | Phobic/Philic |
| 10 | 14 | Cowles | 300 | 10 | 9 | 0 | Phobic |
| 3 | 15 | Prop | 1200 | 10 | 7.7 | 0 | Phobic/Philic |
| 28 | 16 | Cowles | 1200 | 10 | 9 | 1 | Phobic |
| 30 | 17 | Cowles | 300 | 300 | 9 | 1 | Phobic |
| 4 | 18 | Cowles | 1200 | 10 | 7.7 | 0 | Phobic |
| 13 | 19 | Prop | 300 | 300 | 9 | 0 | Phobic |
| 6 | 20 | Cowles | 300 | 300 | 7.7 | 0 | Phobic |
| 14 | 21 | Cowles | 300 | 300 | 9 | 0 | Phobic/Philic |
| 23 | 22 | Prop | 1200 | 300 | 7.7 | 1 | Phobic/Philic |
| 25 | 23 | Prop | 300 | 10 | 9 | 1 | Phobic |
| 12 | 24 | Cowles | 1200 | 10 | 9 | 0 | Phobic/Philic |
| 2 | 25 | Cowles | 300 | 10 | 7.7 | 0 | Phobic/Philic |
| 27 | 26 | Prop | 1200 | 10 | 9 | 1 | Phobic/Philic |
| 18 | 27 | Cowles | 300 | 10 | 7.7 | 1 | Phobic |
| 8 | 28 | Cowles | 1200 | 300 | 7.7 | 0 | Phobic/Philic |
| 32 | 29 | Cowles | 1200 | 300 | 9 | 1 | Phobic/Philic |
| 21 | 30 | Prop | 300 | 300 | 7.7 | 1 | Phobic |
| 19 | 31 | Prop | 1200 | 10 | 7.7 | 1 | Phobic |
| 26 | 32 | Cowles | 300 | 10 | 9 | 1 | Phobic/Philic |

## Appendix 2—Microflocculation Design Results

| Std | Run | Response Ease of Filtration (Min) | Response Retained % Filtrate | Response Viscosity CPS | Response Gloss 20 Deg | Response Appearance 5 = best | Response Clev Hum 10 = best | Response Salt Spray 10 = best | Response Cycl Pro/QUV 10 = best |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 1 | 70 | 19 | 410 | 66 | 5 | 9 | 5 | 7 |
| 16 | 2 | 9 | 15 | 325 | 63 | 5 | 9 | 5 | 7 |
| 1 | 3 | 70 | 20 | 680 | 64 | 4 | 9 | 4 | 7 |
| 22 | 4 | 1.3 | 12 | 55 | 38 | 4 | 1 | 5 | 7 |
| 15 | 5 | 2.5 | 12 | 180 | 28 | 4 | 2 | 5 | 7 |
| 20 | 6 | 1.8 | 11 | 450 | 38 | 3 | 1 | 5 | 7 |
| 24 | 7 | 6.75 | 14 | 70 | 40 | 5 | 2 | 5 | 6.5 |
| 5 | 8 | 6.5 | 15 | 275 | 30 | 4 | 2 | 5 | 7 |
| 29 | 9 | 1 | 12 | 40 | 42 | 4 | 1 | 5 | 7 |
| 17 | 10 | 2 | 14 | 350 | 42 | 3 | 2 | 5 | 6.5 |
| 11 | 11 | 17 | 17 | 195 | 47 | 5 | 9 | 5 | 7 |
| 31 | 12 | 1.66 | 11 | 130 | 56 | 4 | 2 | 5 | 6.5 |
| 9 | 13 | 6 | 14 | 180 | 31 | 4 | 2 | 5 | 7 |
| 10 | 14 | 9 | 17 | 340 | 74 | 5 | 9 | 5 | 7 |
| 3 | 15 | 1.7 | 12 | 185 | 31 | 3 | 2 | 5 | 7 |
| 28 | 16 | 4 | 14 | 125 | 65 | 2 | 3 | 5 | 6 |
| 30 | 17 | 4.5 | 15 | 165 | 66 | 4 | 3 | 5 | 7 |
| 4 | 18 | 75 | 18 | 400 | 72 | 5 | 9 | 5 | 6.5 |
| 13 | 19 | 10 | 15 | 235 | 67 | 4 | 9 | 5 | 6.5 |
| 6 | 20 | 80 | 19 | 580 | 60 | 5 | 9 | 5 | 6.5 |
| 14 | 21 | 0.75 | 11 | 265 | 31 | 5 | 2 | 5 | 7 |
| 23 | 22 | 1.4 | 13 | 170 | 24 | 4 | 1 | 5 | 7 |
| 25 | 23 | 4 | 12 | 95 | 67 | 2 | 2 | 4 | 6.5 |
| 12 | 24 | 3.5 | 11 | 150 | 29 | 5 | 2 | 5 | 7 |
| 2 | 25 | 7.5 | 13 | 210 | 29 | 5 | 2 | 5 | 7 |
| 27 | 26 | 1.1 | 12 | 25 | 40 | 5 | 1 | 5 | 6.5 |
| 18 | 27 | 8 | 14 | 245 | 37 | 4 | 2 | 5 | 6.5 |
| 8 | 28 | 4.75 | 14 | 280 | 33 | 4 | 2 | 5 | 7 |
| 32 | 29 | 1.5 | 12 | 35 | 44 | 4 | 1 | 5 | 6.5 |
| 21 | 30 | 4.5 | 13 | 255 | 43 | 5 | 2 | 5 | 6.5 |
| 19 | 31 | 8.6 | 13 | 255 | 31 | 5 | 2 | 5 | 6.5 |
| 26 | 32 | 2.5 | 12 | 35 | 36 | 4 | 2 | 5 | 6.5 |